QUANTITATIVE

ANALYSIS

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QUANTITATIVE ANALYSIS.

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BY

ALEXANDER CLASSEN,

Director of the Laboratory of Inorganic Chemistry and Electro Chemistry in the Royal Technical School, Aachen.

AUTHORIZED TRANSLATION
FROM THE
FIFTH GERMAN EDITION.

With an Appendix on the Qualitative Analysis of Minerals, Ores, Slags, Metals, Alloys, Etc., Including the Rare Elements.

BY

NORMAN F. HARRIMAN,

Assistant in Chemistry in the University of Michigan.

WITH SEVENTY-NINE ILLUSTRATIONS.

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PREFACE.

The success of Prof. Classen's work in the original, together with the fact that the English Edition published in 1878 is now out of date, seem to make a new English Edition of this valuable work desirable. The work is very extensively used in the Universities and Technical Schools of Germany, and translations have appeared in the French, Russian and Polish languages.

Prof. Classen's arrangement of the matter in the work—advancement from simple Crystallizable Salts, to Alloys, Minerals, Ores, Slags, Metal, Waters, Etc., of increasing difficulty—seems admirably adapted to the needs of the beginning student. The work is no less suited to the practical chemist. As a general rule, the busy analyst has neither the time, nor, perhaps, the library facilities, for arranging a complete scheme for the analysis of the various substances submitted to him, from the individual determinations so commonly given in works on Quantitative Analysis.

A few additions have been made to the German text, notably the method for the Proximate Analysis of Coal, as recommended by the Committee of the American Chemical Society; Handy's Rapid Volumetric Method for Phosphorus, especially prepared by Mr. Handy for this work; Gooch's Gravimetric Method for Titanium,

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adapted from Dr. W. F. Hillebrand's work on Rock Analysis; Julien's Volumetric Method for Manganese; Mixer and Dubois' Method for the decomposition of Chromite with sodium peroxide; Determination of Carbon in Iron and Steel, by solution in Potassium-Copper Chloride, and Combustion of the Residue, and the Electrolytic Determination of Copper. The Appendix on Qualitative Analysis, while somewhat of an innovation in a work on Quantitative Analysis, will, it is believed, be a valuable addition to the work; it was added with the advice of the Leading Authorities on Mineral Analysis in the United States.

The Translator wishes to acknowledge the assistance he has received from Prof. W. H. Pettee, of the University of Michigan; Prof. F. W. Clarke, Chief Chemist of the U. S. Geological Survey; J. O. Handy, Chief Chemist of the Pittsburg Testing Laboratories, and especially Dr. W. F. Hillebrand, Chemist of the U. S. Geological Survey.

THE TRANSLATOR.

Chemical Laboratory,
University of Michigan,
Sept. 1902.

CONTENTS.

PAGE
Introduction 1
General Operations 4
Calcium Carbonate 21
Copper Sulphate 22
Ferrous Sulphate 24
Barium Chloride 25
Magnesium Sulphate 27
Zinc Sulphate 29
Nickel Sulphate 32
Cobalt Sulphate 33
Separation of Cobalt from Nickel 33
Manganous Chloride 37
Potassium Bichromate 39
Sodium Phosphate 40
Lead Chromate 43
Separation of Iodine from Chlorine . . . 44
Separation of Iodine from Bromine . . . 46
Direct Separation of Iodine, Bromine and Chlorine . . 49
Dolomite 53
Barite 62
Alloy of Copper and Zinc 63
Alloy of Copper and Silver 66
Alloy of Copper, Tin and Zinc 67
Alloy of Tin and Lead 68
Alloy of Nickel and Copper 68
Alloy of Lead and Zinc 70
Alloy of Bismuth and Copper 70
Alloy of Lead and Bismuth 71
Alloy of Copper, Zinc and Nickel 73
Alloy of Tin, Copper, Lead and Zinc . . . 76
Alloy of Tin, Lead, Bismuth and Cadmium . . . 76
Alloy of Tin, Lead, Bismuth and Mercury . . . 78
Alloy of Antimony and Lead 78
Phosphor Bronze 82

Alloy of Copper, Tin, Manganese and Phosphorus . . 83
Alloy of Arsenic and Antimony 89
Alloy of Arsenic, Antimony and Tin . . . 90
Separation of Barium from Strontium . . . 99
Separation of Barium from Calcium . . . 101
Separation of Strontium from Calcium . . . 101
Separation of Barium, Strontium and Calcium . . 102
Separation of Barium, Strontium, Calcium and Magnesium . 103
Separation of Potassium from Sodium . . . 103
Mixture of Potassium Chloride, Sodium Chloride and Magnesium Sulphate 105
Alum 108
Siderite 111
Red Hematite 122
Limonite 127
Clay Iron Ore 127
Magnetite 128
Bog Iron Ore 131
Pyrolusite 131
Psilomelane 135
Tin Ore 140
Sphalerite 141
Calamine and Zinc Silicates 148
Phosphorite 148
Vanadinite 162
Ulexite 164
Boracite 169
Analysis of Silicates 169
Natrolite 174
Prehnite 175
Datolite 176
Olivine 177
Ilvaite 178
Ultramarine 179
Refining Slag 183
Copper and Lead Slags 186
Feldspar 194
Clay 195
Glass 198
Epidote 199
Blast Furnace, Cupola and Bessemer Slags . . 202
Tourmaline 204
Chromite 205
Zircon 209

Pyrite 210
Roasted Pyrites 213
Arsenopyrite 215
Chalcopyrite 215
Nickel or Copper Matte 219
Copper or Lead Speise 222
Pyrargyrite. Proustite 225
Tetrahedrite 226
Furnace Bears 228
Stibnite 232
Bournonite 234
Zinkenite 234
Ullmannite 235
Niccolite 235
Linnæite 236
Cabaltite 236
Glaucodote 236
Cerussite 236
Galenite 237
Wulfenite 241
Pyromorphite 242
Lead Matte 244
Red Lead 244
Cinnabar 246
Molybdenite 249
Bismuthinite 250
Uraninite 251
Wolframite 254
Scheelite 257
Refined Lead 257
Hard Lead 262
Antimony 262
Zinc 263
Black Copper 265
Refined Copper 268
Tin 269
Bismuth 270
Silver 270
Nickel 271
Pig-Iron, Steel, Spiegeleisen, etc. 271
Well, Spring, and River Water 315
Mineral Water 333
Ashes 356
Guano 360

Superphosphates 368
Bone Meal 372
Bone Black 373
Coal 374
Soda Ash 381
Pearl Ash 386
Soap 386
Nitre 387
Gunpowder 388
Analysis of Organic Compounds 389
Qualitative Analysis of Organic Compounds . . 389
Quantitative Analysis of Organic Compounds. Ultimate Analysis 390
Volumetric Analysis 407
Alkalimetry 416
Acidimetry 424
Analysis by Oxidation and Reduction . . . 427
Analysis by Precipitation 454
APPENDIX—Scheme for Qualitative Analysis . . 463
TABLES—Atomic Masses . . . 519
Calculation of the Degree of Hardness of Water 521
Tension of Water Vapor, 10–25 Degrees Centigrade 522
Spec. Grav. corresponding to Degrees Beaume 522
Weight of one Cubic Centimeter of Nitrogen . 524
Sulphuric Acid 526
Nitric Acid 527
Hydrochloric Acid 528
Potassium and Sodium Hydroxides . . 529
Ammonia 530
INDEX 531

ERRATA.

Page 26, line 5 from below, *read* “subchloride of,” *for* “metallic.”
Page 112, line 17 from above, *read* “with” *for* “the.”
Page 200, line 13 from above, *read* “alumina” + ferric oxide,” *for* “alumina.”
Page 276, the upper stop-cock should stand in a vertical, instead of a horizontal, position.
Page 278, line 16 from above, *read* “colored,” *for* “covered.”
Page 300, line 5 from above, *read* “successively” *for* “successfully.”
Page 356, line 3 from below, *read* “for” for “on.”
Page 365, line 4 from above, *read* “retain” *for* “contain.”
Page 390, line 11 from above, *read* “formed” *for* “found.”
Page 390, line 18 from above, *read* “halogens” *for* “halogous.”
Page 409, line 2 from below, *omit* “with.”

INTRODUCTION.

The object of quantitative analysis is the determination of the percentage composition of substances, and this may be attained in various ways. In gravimetric analysis, the percentage composition is ascertained by separating the constituent itself, as such, or by transforming the element to be determined into an insoluble compound of known properties and composition, by the addition of a reagent, and then determining the weight of the new compound in a dry condition. The separation of an element, as such, from its soluble compounds, has heretofore been possible in only a few cases; since the development of Electrolytic Analysis,* this exact as well as simple method is applicable not only to the quantitative determination of a large number of metals, but also to their separation.

In gravimetric analysis, therefore, the elements to be determined, are generally transformed into insoluble compounds and their weight determined. If several elements are contained in a solution, the determination of one of them must be combined with a separation from the others.

Suppose it is desired to determine the amount of silver and copper in a silver coin. A weighed sample is dissolved in dilute nitric acid, the free acid removed by evaporation and the nitrates of silver and copper are dissolved in water to which a few drops of nitric acid have been added; the silver is then precipitated by adding hydrochloric acid or a solution of sodium chloride drop by drop to the solution as long as a precipitate is produced. All the silver is separated as silver chloride and the copper remains in solution. After warming and agitating the liquid the silver chloride is filtered off, the copper salt completely removed from the precipitate by washing with water, and the copper precipitated as hydroxide in the filtrate by heating to boiling and adding potassium or sodium hydroxide.

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* A. Classen,—Quantitative Analysis by Electrolysis. Translated by Herrick and Boltwood.

The silver chloride is gently heated in a tared porcelain crucible and weighed as such, while the copper precipitate is changed to anhydrous copper oxide by igniting in a platinum or porcelain crucible and its weight then determined. A simple calculation gives the amount of silver contained in the silver chloride, and the amount of copper in the copper oxide.

Suppose 0.2564 gram of the silver coin was taken for analysis and the following weights were obtained:

Crucible + Silver Chloride, 20.5436 grams
Crucible, 20.2345 “
Silver Chloride, 00.3091 “
AgCl : Ag. = Wt. AgCl : ×
143.03 107.66 0.3091
× = 0.2325 gram of Silver.
Wt. Sample : Wt. Silver = 100 : ×
0.2564 0.2325
× = 90.68% Silver.
Crucible + Copper Oxide, = 21.3464 grams
Crucible, = 21.3165 “
Copper Oxide, = 0.0299 “
Cu O : Cu = Wt. Cu O : ×
79.26 63.3 0.0299
× == 0.0239 gram Copper.

$$\begin{array}{lcl} \text{Wt. Sample} & : \text{Wt. Copper} & = 100 : x \\ 0.2564 & \ 0.0239 & \\ & & x = 9.32\%\ \text{Copper.} \end{array}$$

From the preceding example it is seen that in gravimetric analysis the quantity is determined from the weight of a new substance produced by a chemical reaction. In volumetric analysis, on the other hand, the quantity is determined by the amount of a reagent necessary to either separate a new substance from the solution or to transform one chemical compound into another. For the volumetric determination of silver, e. g., a definite amount of pure sodium chloride is dissolved in a definite amount of water, and this salt solution is then added from a graduated burette to the silver solution as long as a precipitate of silver chloride is formed. From the number of cubic centimeters of salt solution used the amount of silver may easily be calculated.

$$\text{NaCl} : \text{Ag.} = 58.36 : 107.66.$$

In the filtrate from the silver chloride, the copper may be determined in a similar manner.

GENERAL OPERATIONS.

Among the operations which precede quantitative analysis, the first to be mentioned is pulverization. With substances which are difficultly attacked by solvents, fine division is of the greatest importance, since coarsely pulverized substances offer too few points of attack and dissolve very slowly, or only imperfectly.

The substance should be pulverized in a mortar of porcelain, iron, agate or steel, according to its properties. Steel mortars, also called diamond mortars, are used to pulverize hard minerals, cast iron, etc. The arrangement of this mortar may easily be seen in Fig. 1. The substance to be pulverized is placed in the cavity of the small steel block a, the pestle b is placed in the cylinder and struck with a hammer.* In some cases pulverization in a steel mortar is not sufficient, and it may be necessary to sift or wash out the fine particles and repeat the pulverization until the substance is uniformly fine. To sift a powdered substance, stretch a fine piece of linen over a beaker, place the powder on the cloth, and by lightly tapping the glass the fine particles pass through the cloth into the beaker. The course powder remaining

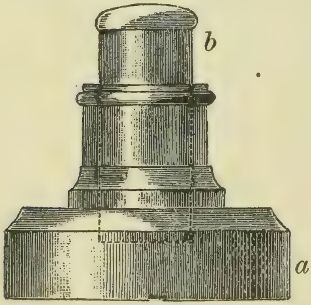

Fig. 1.

[* Dr. W. F. Hillebrand, Chemist of the U. S. Geological Survey, recommends the use of a hardened steel anvil about 4.5 cm. in thickness by 10 cm. square, and a hammer with a hardened steel face for pulverizing minerals with a minimum of contamination. A steel ring 2 cm. high and 6 cm. inner diameter, prevents the fragments being scattered. Bull. 176, U. S. Geol. Surv.]

on the linen is pulverized as before and the operation repeated until no residue remains on the linen. Substances which contain constituents that are soluble in water or are oxidizable in a moist condition, can not be pulverized in the presence of water. If the substance is insoluble in water, it is placed in a mortar, some water is added and the mixture is then ground with a pestle, allowed to stand quietly for a few minutes and the liquid carefully poured off into a beaker. The powder remaining behind is further pulverized with the pestle and the washing with the water repeated. When the substance has settled in the beaker, the water is carefully poured off and the residue dried in the air-bath.

To remove hygroscopic moisture, all substances must be dried before weighing.

Crystallized salts which lose their water of crystallization on exposure to the air, or effloresce, are freed from hygroscopic moisture by pressing the fine powder between filter paper. Substances which are changed by heating to 100° C. are dried in the dessicator. Concentrated sulphuric acid is the best drying agent for use in dessicators. The porcelain dish in Fig. 2 is partially filled with sulphuric acid. The substance to be dried is placed on the ring r, and the bell glass g is pressed tightly on the ground glass plate p.

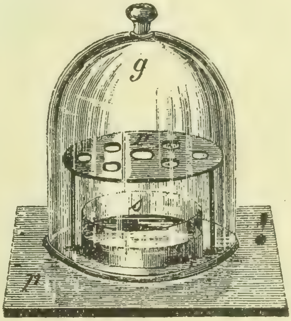

Fig. 2.

Portable dessicators which are used to cool hot crucibles or dishes before weighing, have the form shown in Fig. 3.

Substances which are not decomposed by a temperature over

100° C., such as minerals, certain organic compounds and salts, are always dried to constant weight in an air- or oil-bath at 100° C.

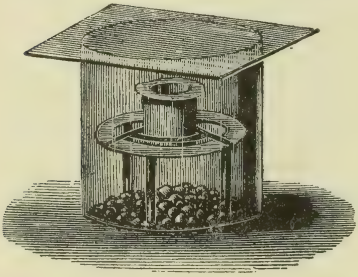

Fig. 3.

This apparatus should be provided with a thermometer and a thermostat in order to maintain any desired temperature.

Fig. 4 shows the arrangement of such an apparatus.

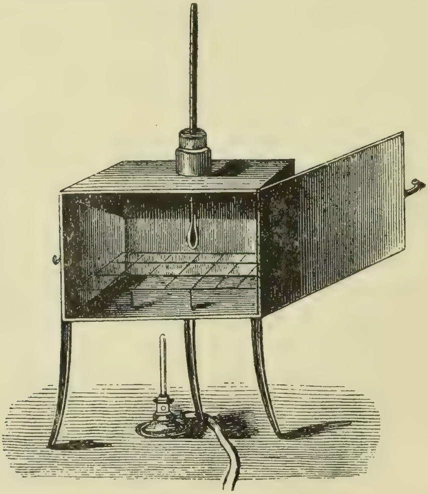

Fig. 4.

To heat substances at a definite temperature in a current of gas, or to separate volatile from non-volatile substances, e.g., sulphur mixed with metallic sulphides, the drying oven shown in Fig. 5 is used.

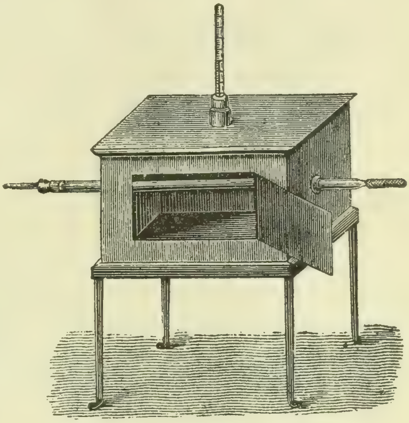

Fig. 5.

The dried substance is cooled in a dessicator before weighing. For this purpose a quantity is placed in a dry weighing bottle, which should be closed with a ground glass stopper, Fig. 6; the latter is placed on the left pan of the balance and its weight determined. A portion of the substance is placed in the vessel in which solution is to be effected, and the bottle reweighed. The difference between the two weights expresses the amount of the substance taken.

Fig. 6.

The manipulation of the balance is very simple. If the weighing bottle containing the substance is placed on the left pan of the balance, a weight approximately equal to that of the substance should be placed on the right hand pan, e.g., 10. grams. After lowering the beam arrest, if the pointer swings to the left, the weight is too heavy; the arrest is again raised and the next smaller weight, 5 grams, is placed on the pan. If the pointer now swings to the right, first the 2. gram weight, and in case that is too heavy, the 1. gram weight is placed on the right pan, always after previous arrest of the beam. If the pointer still swings to the right, the weight is between 6. and 7. grams. Continue in this manner by adding 0.5, 0.2 or 0.1 gram to determine the tenths of a gram. If, for example, 0.5 gram is too heavy and 0.4 gram too light, the true weight lies between 0.4 and 0.5 gram. Then add 0.05 gram, and if the pointer swings to the right, 0.02 or 0.01 gram, etc. If 0.01 e.g. causes the pointer to swing to the right, the remaining milligrams are still to be determined. It is not advisable to place on the pan, weights smaller than 10 milligrams, but it is more convenient to determine the milligrams and tenths of milligrams with the rider. The rider is placed on the beam at e. g. 4. mg., the arrest lowered and the beam allowed to swing, after closing the balance case. Now observe whether the pointer swings an equal number of divisions either side of the zero point. Adjust the rider so that the pointer swings an equal number of divisions on each side of the zero point on the scale.

To avoid errors in writing down the weight of a substance, first add up the weights lacking from the weight box and check this result by adding up the weights on the pan. It must not be forgotten that vessels must be perfectly cool before being weighed, since by radiation of heat the pan is raised and the weight found will be too small.

After the substance has been weighed, it is dissolved in a suitable solvent.

Substances soluble in water are dissolved directly in the beakers in which the precipitation is to be made. Substances which must be decomposed by digestion with acids are warmed on the sand-bath or water-bath in a covered casserole until decomposition is effected. The excess of acid is evaporated, either on the steam-bath or water-bath. Figs. 7 and 8 show this apparatus.

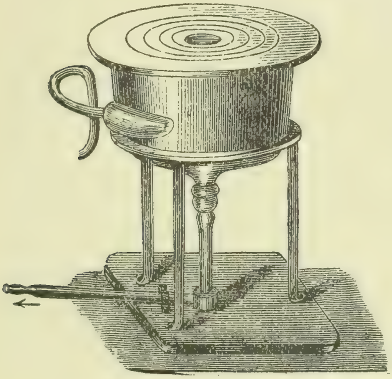

Fig. 7.

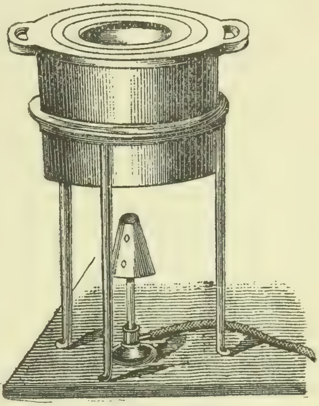

Fig. 8.

In order to protect the liquid from impurities, Victor Meyer has devised the apparatus shown in Fig. 9.

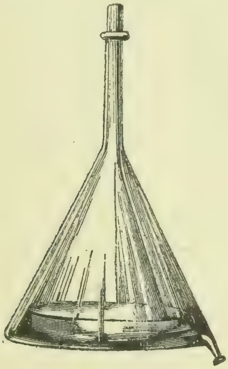

Fig. 9.

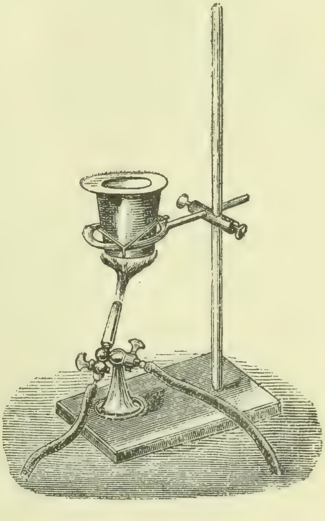

Fig. 10.

Substances which are slightly or not at all attacked by acids, are generally fused in a platinum crucible with potassium-sodium carbonate, using a blast lamp, Fig. 10.

After complete decomposition, pour on a platinum foil or into a platinum dish. If this method has been used to decompose a silicate insoluble in acids, e. g. glass, feldspar, etc., place the cooled mass together with the crucible in a platinum or porcelain dish, add a small amount of distilled water, cover with a watch glass and gradually add dilute hydrochloric acid.

When effervescence ceases, all carbonates are changed into chlorides. Rinse off the watch glass with a wash-bottle, Fig. 11., remove the crucible from the liquid with a glass rod and wash it repeatedly with water until perfectly free from the solution.

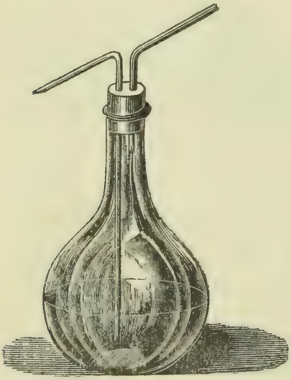

Fig. 11.

As explained in the introduction, gravimetric analysis consists either in separating, as such, the constituent to be determined, or in transforming it into an insoluble compound of definite composition.

The manipulation most frequently occurring in quantitative analysis, is precipitation. This is generally done in beakers. The use of the latter is always excluded when alkaline hydroxides or carbonates must be used, as, for example, in the precipitation of the hydroxide of iron, aluminum, chromium, nickel or cobalt, by ammonium, potassium or sodium hydroxide, since these reagents strongly attack glass, especially when hot, and thus bring foreign matter into the solution.

For such precipitations, platinum or porcelain dishes are used. A general rule as to how precipitations can best be executed, cannot be given, since in some cases an excess of the reagent is necessary, and in other cases an excess is injurious. For example, aluminum and chromium cannot be precipitated as hydroxides with potassium- or sodium hydroxide, since both precipitates are easily soluble in an excess of the precipitant. For this reason, ammonium hydroxide is used, and the latter added only in slight excess, since the hydroxides of these metals are not entirely insoluble in this reagent. The excess of the ammonia is removed by boiling the solution. When the precipitation is complete, the supernatant liquid is separated from the precipitate. Under no conditions is it advisable to filter until the precipitate has completely settled and the liquid appears perfectly clear. In many cases, standing for several hours is necessary to effect a quantitative separation. Thus, magnesium-ammonium phosphate, cobalt-potassium nitrite, potassium-platinic chloride, ammonium phospho-molybdate and the oxalates of magnesium, zinc, manganese, cobalt and nickel, form only gradually, and for complete precipitation require to stand for about 6 hours. With cobalt-potassium nitrite, 24 hours are necessary for complete separation.

Precipitates are separated from the liquid by filtration. Those precipitates which are contaminated by the adsorption of the precipitant, e. g., all precipitates produced by alkaline hydroxides or alkaline carbonates, should be washed be decantation. The clear liquid is decanted through a filter, a fresh quantity of distilled water is poured over the precipitate in the beaker, and the operation repeated until no fixed constituent is recognizable in the filtrate. This manner of purification of precipitates has the great inconvenience that the filtrate is very much diluted, so that if other constituents are to be determined, the solution must be concentrated by evaporation. The method also presupposes the complete insolubility of the precipitates in large quantities of water, which is never the case. It is much more simple to remove the adhering liquid by suction, and to continue the washing in the same manner. This latter method is especially to be recommended if the precipitates are voluminous, such as iron, aluminum, and chromium hydroxides, or are not entirely insoluble, such as ammonium-magnesium phosphate, and potassium-platinic chloride. For this purpose, a funnel of exactly 60°, and a platinum cone, are necessary. Bunsen, who introduced this excellent method, describes the preparation of the platinum cone in the following words.* "A piece of writing paper is accurately fitted to a carefully selected glass funnel and cemented on its upper edge by a few drops of sealing wax. It is then saturated with oil and filled with a paste of plaster of Paris, and while the paste is still soft a small stick is inserted for a handle. After a few hours, the cone, exactly corresponding to the funnel, may be taken out by the handle. Fill a crucible 4-5 cm. high with plaster of Paris such as was used before, and press the cone with its oiled paper down into the soft mass. After the latter has hardened, remove the paper by gently rubbing with the finger. There is thus obtained a cone and a hollow cone which exactly correspond to the walls of the funnel. To make a platinum cone from the plaster cones, cut a piece of platinum foil of the form shown in its natural size in Fig. 12. After the foil has been softened by heating, the cone is laid so that its apex is at c, press the flap c, d, b, close to the cone, rotating with pressure. The platinum cone should allow no light to pass through its apex, and will possess, without soldering, sufficient strength for all purposes.''

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* Ann. Chem. Phar., Vol. 148, p. 129.

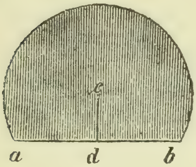

Fig. 12.

To filter by suction, the platinum cone is placed in a funnel, a filter accurately fitted to the latter,* and the stem passed about 6 cm. through a rubber stopper which fits a suction flask of suitable size. In place of the stopper, a piece of rubber with an opening for the funnel, may be tightly stretched over the mouth of the suction flask. Figs. 13 and 14 show the arrangement. The air is exhausted by means of an aspirator, the connection being made with a rubber tube. A much greater difference of pressure and quicker filtration can be obtained by using a water pump.

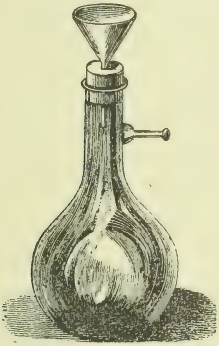

Fig. 13.

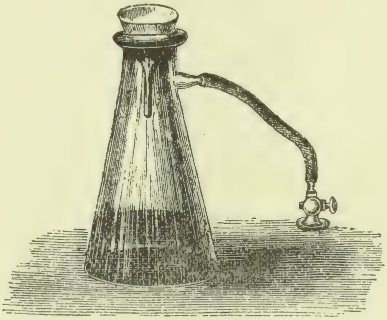

Fig. 14.

Since the introduction of Bunsen's pump, a number of similar contrivances, more or less perfect, have been constructed.

If it is desired to avoid the use of filter paper, e. g., with precipitates which are easily reduced by the carbon of the paper, (see page 20), the Gooch crucible may be used.

---

* Press the filter tightly into the apex of the cone with the finger, moisten with water, and press tightly to the walls of the funnel so that no bubbles of air can circulate between the funnel and filter.

This crucible, commonly made of porcelain or platinum, is of the ordinary size, but does not taper much toward the bottom, and the latter is pierced with fine holes and is covered with a layer of asbestos in the following manner: Select soft, long-fibered asbestos, cut it into small pieces, boil with hydrochloric acid, transfer to a fine-meshed sieve with water and then wash until all fine particles are removed.

The crucible is set in a glass tube which is wide enough at its upper end to admit the crucible a third of its height. Cut a piece of thin-walled rubber tubing of such a size that when stretched over the joint it will make it air tight. The lower end of the tube should be of the same size as a funnel stem, so that it can be used with the suction flask described above. A Woulff's flask with three necks should be interposed between the suction flask and the pump; in one of the necks, a glass stop-cock should be placed.

Connect the pump, and pour water with the asbestos in suspension in a fine stream into the crucible until the layer of asbestos will allow no light to be seen through the holes in the bottom. Place a piece of platinum foil on top of the asbestos to avoid disturbing the layer. The crucible must now be weighed. For this purpose, place the cap on the bottom, warm carefully to expell the moisture, and then ignite a few minutes over the blast lamp. After cooling in the dessicator, determine its weight.

To make a filtration, again fasten the crucible in the suction apparatus, first pour the clear solution through with gentle suction, and finally transfer the precipitate to the crucible with the wash water. During washing, gentle suction should be used so as to allow the wash water to exert its solvent effect upon the impurities that are to be removed, and also to avoid the excessive dilution of the filtrate. The precipitate must always be covered with liquid, otherwise it is too tightly packed and is difficult to wash. To test the filtrate for substances that are being washed out, carefully relieve the vacuum by the glass cock in the Woulff's bottle, while the crucible is still half full of wash water. If the washing is completed, replace the crucible and suck the precipitate as dry as possible. Place the cap on the bottom, dry in the air-bath (see page 6), cover, ignite at first gently, and then increase the temperature according to the nature of the precipitate.

In certain filtrations, e. g. with silver chloride, a tube shown 1/2 natural size in Fig. 15, may be used. The tube is prepared by Jannasch in the following manner: In the lower part a, place a layer of glass wool about half a centimeter thick without allowing it to get into the narrow part of the tube and upon this an equal layer of asbestos, which has been purified as described above. Wash with water until all particles of glass wool or asbestos are washed out. The tube, open at both ends, is dried in the drying oven at about 150°C., allowed to cool to about 50–60°C., and then closed with the glass caps. After cooling in the dessicator, it is weighed. A small funnel may be used in pouring the solution into the tube.

Fig. 15.

A few remarks may be made as to the quality of filter paper to be used, as well as the manipulation of filters. The filter paper found in commerce under various names, always contains more or less mineral matter, (silica, alumina, ferric oxide, calcium oxide, etc.) which is partially soluble on treating with dilute acids. It is self evident that such papers cannot be used for accurate analysis without being further treated to remove the soluble constituents. The purification of filter papers is best done by placing the cut filters in a platinum dish, digesting in the cold for several days with equal parts of hydrochloric and hydrofluoric acids. The paper should then be washed with water until the acids are removed. The washed paper is dried in a platinum dish on the water-bath.

For technical analysis, it is sufficient to determine the amount of ash, and substract this from the weight of the precipitate. For this purpose, weigh a platinum crucible, successively incinerate 12 filter papers from different parts of the package, and allow the ash to fall into the crucible. Weigh the residue, and divide the gain in weight by 12, to obtain the weight of ash of one paper. The size of the filter paper chosen should depend exclusively on the amount of the precipitate and not on the volume of the solution to be filtered. The larger the surface of the paper, the more liquid is required to wash the precipitate, and the filter is incinerated with more difficulty.

In filtering, a glass rod should always be used, and the current directed to one side of the filter. The under side of the lip of the beaker should be covered with a film of tallow, to prevent the solution running down the side of the beaker. The filter should never be filled more than two-thirds full with the liquid. The precipitate should not be brought onto the filter until the greater portion of the solution has been filtered, as the precipitate clogs the pores of the filter. The precipitate may be washed onto the filter by the aid of the wash-bottle.

When the precipitate consists of sulphides which oxidize easily in the air, as copper sulphide, it is necessary to exclude the air as much as possible by placing watch glasses on the funnel and beaker. Hydrogen sulphide water should be used to wash such precipitates to prevent their oxidation. In some cases, as with zinc sulphide, ammonium nitrate should be added to the wash water. If suction is used in the filtration, as much of the liquid as possible should be sucked from the precipitate so that the latter packs together. The washing should be continued until the precipitate is free from the solution. A few drops of the filtrate evaporated on platinum foil will leave no residue if all impurities have been washed from the precipitate. Reactions of substances in the filtrate are often used to indicate when the washing is complete, e.g., the presence of hydrochloric acid or chlorides in the filtrate, is tested for by silver nitrate. In the separation of copper from nickel by precipitation of the former as cuprous sulphide, the purity of the precipitate may be ascertained by testing a few drops of the filtrate with ammonium hydroxide; the presence of nickel is indicated by a cloudiness due to nickel sulphide.

The method of washing a precipitate varies with its properties. With the exception of sulphides, most precipitates are washed with distilled water, to remove impurities. Some compounds require a special reagent for their quantitative separation, consequently these precipitates require special washing solutions. Ammonium-magnesium phosphate, which is precipitated in an ammoniacal solution, must be washed with dilute ammonium hydroxide; potassium-platinic chloride is insoluble only in alcohol and must therefore be washed with the latter. Ammonium phospho-molybdate must be washed with either ammonium molybdate or ammonium nitrate, etc.

The further treatment of precipitates in their gravimetric determination likewise depends upon their special properties. Compounds which volatilize or decompose on ignition require special treatment. Such precipitates are collected on a dried and weighed filter, dried in the air-bath at 110° C. to 120° C., and weighed with the filter.

To prevent the absorption of moisture during weighing, the empty filter as well as the filter with the precipitate should be dried between two close-fitting watch glasses, which may be held together by a spring clamp. Or, the filter may be dried to constant weight in a large weighing bottle with a ground stopper. A weighing bottle for drying filters, proposed by Reinhardt, is shown in Fig. 16.

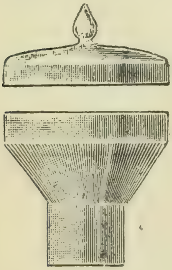
Fig. 16.

The filter is first partially dried in the funnel so that it may be removed without tearing and is then placed in the weighing bottle. This form of bottle is especially suitable for sulphide precipitates. Compounds which are not reduced by the carbon of the paper may be ignited directly, heating gently at first, then more strongly. Fold the upper edge of the filter towards the center, place in the crucible, cover, and heat with a small flame as long as volatile matter is given off. The crucible should then be inclined and the cover placed at an angle against the top, and then heated at a strong heat to burn off the remaining porous carbon.

Precipitates that are easily reduced must be carefully separated from the filter. The precipitate is transferred as much as possible to the crucible and the little that adheres to the paper is removed by gently rubbing the filter between the fingers. The filter is then burned on the inverted crucible cover, finally heating it at a sufficiently high temperature to completely burn all the carbon.

If lead sulphate is thus treated, the carbon of the paper reduces the adhering precipitate to metallic lead, and the latter must be changed to sulphate. For this purpose, moisten the residue on the crucible cover with a few drops of nitric acid, warm gently, and after solution of the lead, add a few drops of dilute sulphuric acid and evaporate to dryness. The excess of sulphuric acid is removed by strongly heating the residue over the flame.

Precipitates that are easily reduced cannot be ignited in a platinum crucible, since the reduced metal at once alloys with platinum and destroys the crucible.* Ammonium-magnesium phosphate is also easily reduced to phosphide in the presence of carbon at a high temperature. Whether a precipitate should be ignited gently or strongly, depends upon its properties; a temperature of about 120° C. is sufficient for silver chloride, while silica separated from silicates must be strongly ignited with the blast

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* With reference to the preservation of platinum crucibles, the following points should be observed:—

The hydroxides of the alkalies, lithium chloride, the hydroxides of barium and strontium, and the nitrates of these metals, attack platinum at a red heat and are especially injurious at a white heat.

Still more injurious is a fused mixture of potassium hydroxide and lamp to completely dehyrate it. As a rule, however, ignition at a low red heat is sufficient.*

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potassium nitrate.

The ordinary fusion mixture of sodium carbonate and potassium nitrate slightly attacks platinum at a high temperature. Fused alkaline cyanides also attack platinum.

Sulphur alone, at a red heat, does not attack platinum, but in the presence of the alkalies it is to be avoided, since alkaline sulphates are reduced by carbon.

Contact with chlorine and substances that liberate chlorine, in the molten state as well as in the liquid state, should be avoided.

Platinum crucibles when heated in contact with coal take up carbon and silicon and become brittle.

The surface of a crucible may become blistered and rough by the formation of platinum carbide, if heated in a gas flame with an insufficient supply of air. Scouring with sea sand restores the polish and this should be done after each ignition, if the surface has assumed a dull appearance.

[* On general principles and methods of quantitative analysis, especially as applied to Rock Analysis, see Bull. 176, U. S. Geol. Sur., by Dr. W. F. Hillebrand. This bulletin cannot be too highly recommended to those interested in quantitative analysis.]

CALCIUM CARBONATE.

CALCITE. MARBLE.

$CaCO_3$

Determination of Calcium*:—Dry the substance at 100°C., and dissolve 0.2-0.3 gram in dilute hydrochloric acid in a beaker; dilute with 100.–150 cc. of water. The calcium is precipitated as calcium oxalate. Add ammonium hydroxide to alkaline reaction, and heat the liquid to boiling; now add ammonium oxalate in slight excess, and allow the precipitate to settle for about 6 hours in a warm place. If the ammonium oxalate is added drop by drop with stirring, the calcium oxalate separates as a heavy, pulverulent precipitate.† After the calcium oxalate has been perfectly washed with hot water,‡ it is placed in a platinum crucible without previous drying and ignited to calcium carbonate, or preferably to calcium oxide.

To dry the precipitate and filter, and finally to incinerate the latter, carefully fold up the paper, place in a covered crucible and gently heat with the flame of a Bunsen burner as long as fumes are evolved. Then remove the crucible cover, incline the crucible so as to freely admit air, and heat at the same temperature until the carbon is burned and the residue is white. The calcium oxalate may be transformed to carbonate by very gentle heating;

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* For the determination of Carbon Dioxide see Dolomite.

† This general rule is to be recommended for all precipitations.

‡ The precipitate should be washed until silver nitrate shows the absence of chlorine.

since the latter, however, is easily decomposed into calcium oxide, it is necessary to allow the crucible to cool and then to moisten the residue with a few drops of ammonium carbonate and again heat gently. This operation must be repeated until constant weight is obtained.

If it is desired to determine the calcium as oxide, ignite over the blast lamp for about 5 minutes, cool and weigh; then re-ignite and see if the weight of the precipitate diminishes. Ignite to constant weight.

COPPER SULPHATE.

BLUE VITRIOL.

$CuSO_4+5H_2O$

Determination of Copper as Oxide, CuO:—Dissolve about 1. gram of copper sulphate in about 150 cc. of water in a porcelain dish, and heat to boiling. Gradually add a slight excess of potassium or sodium hydroxide and continue the boiling for a few minutes. After the precipitate has settled, decant off the clear solution, pour hot water over the precipitate, boil again and repeat these operations several times, or until the precipitate is free from alkali.

The precipitate is then brought onto the filter with the aid of the wash bottle and washed with hot water until a few drops of the filtrate leave no residue when evaporated on platinum foil.

The copper oxide may be determined as given under Calcium Carbonate, by placing the moist precipitate and filter in a weighed porcelain crucible and igniting. It should not be forgotten that the carbon of the filter may reduce a part of the copper oxide to metallic copper. The latter may be reoxidized by cooling the crucible and adding a few drops of nitric acid. The excess of the latter is removed by carefully warming and then heating with the flame of a Bunsen burner until constant weight is obtained.

Determination of Copper as Cuprous Sulphocyanate, $Cu_2(CNS)_2$:—Dissolve about 1. gram of copper sulphate in 100 cc. of cold water, add about 50 cc. of water saturated with sulphur dioxide and then gradually add potassium sulphocyanate in slight excess. After the precipitate has completely settled, filter on a filter paper which has previously been dried at 110° C. and weighed. Wash by decantation with cold water until the filtrate shows no cloudiness with silver nitrate. The copper sulphocyanate is dried at 105–110° C. to constant weight.*

The determination of the sulphuric acid depends upon the insolubility of barium sulphate in water and in dilute acids. Dissolve about 1. gram of copper sulphate in 150–200 cc. of water, and 5.–10. cc. of dilute hydrochloric acid and heat to boiling; stir constantly and add barium chloride, drop by drop, until in slight excess.

Proceed according to the directions given for the precipitation of calcium oxalate. As soon as the precipitate has settled, filter, and wash with hot water until the filtrate gives no test for chlorine with silver nitrate. Treat the precipitate as usual. Since the barium sulphate may be slightly reduced to sulphide by the carbon of the filter, cool and moisten with a few drops of nitric acid, and ignite for a short time with access of air.

Determination of Water of Crystallization:—Heat a weighed quantity of the copper sulphate in the air-bath at

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* The precipitate dries very slowly, and may, under certain conditions, reqire 12 hours to remove all the moisture.

120° C. for some time, and then carefully heat with a Bunsen burner until the weight of the residue is constant. The bottom of the crucible should be heated to only a low red heat, to avoid the decomposition of the anhydrous copper sulphate.

FERROUS SULPHATE.

GREEN VITRIOL.

$FeSO_4+7H_2O$

Determination of Iron :—Dissolve about 1. gram of the air-dried salt in water, add hydrogen peroxide or nitric acid, and heat to oxidize the ferrous iron to ferric. When the solution has assumed a yellowish-red color, add ammonium hydroxide in slight excess and warm for some time on the water-bath. Wash the precipitate with hot water by decantation, dry, and ignite as usual in a porcelain or platinum crucible. It is advisable to moisten the ignited precipitate with a few drops of nitric acid and repeat the ignition.

The sulphuric acid may be determined in the filtrate from the ferric hydroxide.

Acidify with hydrochloric acid, boil, and precipitate with barium chloride. If sulphuric acid is precipitated directly in the presence of ferric iron, the precipitate is contaminated with the latter. However, the solution containing iron may be heated nearly to boiling, precipitated with ammonium hydroxide, and barium chloride at once added. The ferric hydroxide may then be dissolved by moderately acidifying with hydrochloric acid. Allow to stand warm for 2 hours, then cool and filter without bringing the precipitate onto the filter. Digest the precipitate for half an hour with 30 cc. of boiling water and 2 cc. of hydrochloric acid, decant, and repeat the operation 3 times; finish the washing on the filter. The barium sulphate is determined as given under Copper Sulphate.

The water of crystallization cannot be determined by direct ignition in a crucible, since the ferrous iron is gradually oxidized to ferric iron. The heating must be done in the absence of air. For this purpose weigh a small glass bulb of difficultly fusible glass,* place in it .5 gram of the substance and weigh again. The tube of the bulb is now drawn out to a small opening about 2 cm. from the bulb and at the same time bent over in the form of a retort. Gently heat the contents of the bulb until all water is expelled from the stem.† When the water vapor is all expelled, fuse together the tip of the tube while the contents are still hot and allow the bulb to cool. After cooling, break off the point and reweigh the bulb and broken tip.‡

BARIUM CHLORIDE.

$BaCl_2+2H_2O$

The barium is weighed as carbonate or sulphate. To determine it as carbonate, dissolve from 0.5 to 1.0 gram in water, add ammonium carbonate in slight excess and warm gently for some time on the sand-bath. Wash the precipitate with dilute ammonium hydroxide, and ignite gently over the Bunsen burner.

To determine the barium as sulphate, acidify the solution with hydrochloric acid and precipitate with dilute sulphuric acid. See Determination of Sulphuric Acid in Copper Sulphate.

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* These bulbs are easily prepared by blowing a small bulb on the end of a tube of difficultly fusible glass.

† The ferrous sulphate loses all its water at about 280° C.

‡ For the direct determination of moisture, see Dolomite.

Determination of Chlorine :—Warm the solution, and add silver nitrate acidified with nitric acid.* Stir the solution with a glass rod until the silver chloride collects together and the supernatant liquid is clear. Decant the liquid through the filter and wash the silver chloride by decantation with hot water slightly acidified with a few drops of nitric acid, until the solution shows no trace of silver ; finally bring the precipitate onto the filter. After drying, transfer the silver chloride as much as possible to a porcelain crucible and incinerate the filter on the inverted crucible cover. Particles of silver chloride adhering to the filter are reduced to metallic silver, and must again be changed to silver chloride. After cooling, moisten the ash with a few drops of nitric acid, warm gently, and add a drop or two of hydrochloric acid.

Carefully evaporate the acids, place the cover on the crucible and heat the latter until the contents just begin to fuse. Instead of transferring the silver chloride to a porcelain crucible, it may be collected on a filter which has previously been dried at 130° C., and weighed. The precipitate should then be dried at the same temperature to constant weight. Silver chloride is easily darkened by bright sunlight, owing to partial reduction to metallic silver ; precautions must therefore be taken to avoid unnecessary exposure.

The silver chloride may also be filtered in the asbestos tube described on page 15. After the precipitate has been washed, dry the tube at 150–200° C. and then weigh.

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* The solution should not be acidified with nitric acid before adding the silver chloride, as hydrochloric acid might be volatilized.

Determine the water of crystallization by gently igniting a weighed sample of the salt.

MAGNESIUM SULPHATE.

$MgSO_4+7H_2O$

Determination of Magnesium :—Dissolve 1.–1.5 grams of the air-dried salt in about 50 cc. of water ; add ammonium chloride and then one-third the volume of ammonium hydroxide. If a sufficient amount of ammonium chloride has been added, no precipitate of magnesium hydroxide will be produced ; otherwise add ammonium chloride until the resulting precipitate is dissolved. To the clear solution, add sodium-ammonium phosphate,* drop by drop and with constant stirring, which produces a white, crystalline precipitate of ammonium-magnesium phosphate. When the supernatant liquid is clear, filter off the precipitate and wash it with a mixture of 1 part of ammonium hydroxide, Sp. Gr. .96 and 3 parts of water, until no test can be obtained for chloride in the filtrate.

Dry the precipitate, remove it as much as possible from the filter, and place in a porcelain crucible† with the ash of the filter which has previously been incinerated on the inverted crucible cover. Moisten the precipitate and filter-ash with nitric acid and ignite for some time at a gentle heat, and then at a full red heat, until constant weight is obtained. If, after ignition, the color of the precipitate is not pure white, moisten again with nitric acid and re-ignite. The residue is magnesium pyrophosphate, $Mg_2P_2O_7$.

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* If sodium phosphate is used as the precipitant, the solution must be allowed to stand at least 12 hours for the complete separation of the precipitate.

† It is not advisable to use a platinum crucible for the ignition as the phosphoric acid may be reduced and attack the platinum.

Determination of Magnesium as Magnesium Oxide[*] :—Magnesium salts in neutral or weakly acid solutions,[‡] with ammonium oxalate form soluble magnesium-ammonium oxalate, which is decomposed by the addition of concentrated acetic acid, and magnesium oxalate is precipitated. To precipitate magnesium quantitatively as oxalate, dissolve 1.–1.5 grams of the substance in about 25. cc. of water, and add either a solution of ammonium oxalate, or 1.5–2.0 grams of the solid salt.[‡] Heat to boiling and then gradually add an equal volume of concentrated acetic acid[‖] and boil for a minute, with constant stirring. If the quantity of magnesia is not too small, the addition of the acetic acid produces a heavy, crystalline precipitate of magnesium oxalate, which quickly settles to the bottom of the beaker on removal of the flame. Small amounts of magnesium are only precipitated after standing for some time. In all cases, the solution should be covered and allowed to stand for at least 6 hours at about 50° C. Filter, and wash the precipitate with a solution of equal parts of concentrated acetic acid, alcohol and water. Ignite the magnesium oxalate to magnesium oxide, in a platinum crucible. To avoid any loss, fold up the moist filter containing the precipitate ; heat the covered crucible gently at first and proceed as directed in the

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[*] Classen, Zeit. f. anal. Chem. Vol. 18, p. 373.

[†] If the solution to be precipitated contains free acid, the latter must be removed by evaporation, otherwise compounds are formed which are not quantitatively precipitated by acetic acid.

[‡] If a sufficient amount of ammonium oxalate is present, a clear solution results. If a precipitate forms, add enough of the reagent to form the soluble double salt.

[‖] When the precipitate has settled, test for further precipitation with a little more acetic acid.

Determination of Calcium, page 21.*

The sulphuric acid may be determined as given under Copper Sulphate, page 23.

The water of crystallization of the salt may be determined by drying a weighed amount at 210° C., to constant weight.

ZINC SULPHATE.

WHITE VITRIOL.

$ZnSO_4+7H_2O$

Determination of Zinc as Zinc Oxide :—Dissolve about 1.0 gram of the salt in water in a porcelain or platinum dish†, heat to boiling and gradually add sodium carbonate in slight excess. Continue the boiling for a few minutes, decant off the clear liquid, pour hot water on the precipitate and boil again. These operations must be repeated until a drop of the filtrate leaves no residue when evaporated on platinum foil. Place the moist precipitate and filter in a weighed platinum crucible and ignite as given under Calcium Carbonate. Finally heat the crucible to a low red heat to change the zinc carbonate into zinc oxide.

The zinc oxide should be tested for alumina and silica.

Second Method :—The preceding method has many disadvantages. If the precipitation is not made in a platinum vessel, the zinc carbonate always contains appreciable

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[*] The magnesium oxalate should be heated gently at first, in a covered crucible, and the temperature gradually raised. If the crucible is heated too rapidly, the gases carry out particles of the precipitate.

[†] If vessels of glass or inferior porcelain are used for the precipitation, the zinc carbonate always contains silica and alumina. Dissolve the ignited precipitate in hydrochloric acid, filter, and add ammonium hydroxide in slight excess.

amounts of the constituents of the porcelain, besides, the complete removal of the sodium carbonate from the precipitate is a very tedious operation. It is much quicker to precipitate the zinc as oxalate and then ignite to the oxide.* Add to the water solution, which should be neutral or weakly acid† and about 20-25 cc. in volume, sufficient neutral potassium oxalate (1 part potassium oxalate to 3 parts of water) to re-dissolve the precipitate of zinc oxalate. Heat to boiling and gradually add concentrated acetic acid,‡ stir, and continue boiling for some time.

The quantity of acetic acid must be at least equal to the volume of the solution. (See Determination of Magnesium as Oxide.) After standing for about 6 hours at 50° C., filter, and wash the precipitate with equal parts of alcohol, acetic acid and water, until a drop of the filtrate leaves no residue when evaporated on platinum foil. The zinc oxalate is ignited to zinc oxide as given above. If the precipitate is not sufficiently washed, it is contaminated with potassium carbonate, which may easily be detected by moistening the precipitate and testing with litmus paper. If the precipitate has an alkaline reaction, digest for some time on the water-bath or sand-bath and then remove the last traces of the alkali by filtering off the zinc oxide and washing with hot water. Ignite and weigh.

Determination of Zinc as Zinc Sulphide :—Zinc may be separated as zinc sulphide either by ammonium sulphide or by hydrogen sulphide. The precipitate thrown down by ammonium sulphide is of a slimy nature, and is much more difficult to filter and wash than that produced by hydrogen sulphide. For the first method, add ammonium nitrate* to the dilute solution, then add ammonium hydroxide until the resulting precipitate is redissolved; heat to boiling and add ammonium sulphide in slight excess. Allow to stand in a warm place until the zinc sulphide has settled. Wash the precipitate by decantation, as the zinc sulphide clogs the filter. Use a dilute solution of ammonium nitrate for the washing liquid.

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* Classen, Zeit. f. anal. Chem Vol. 18, p. 189.

† This method for the separation of zinc presupposes as neutral solution as possible. Free acid must be completely removed by evaporation.

‡ See note ||, page 28.

To precipitate zinc with hydrogen sulphide, add sodium acetate in slight excess to the water solution,† add a few drops of acetic acid, heat to boiling and pass hydrogen sulphide until the liquid is completely cold. Filter, and wash the precipitate with water containing ammonium nitrate.

The zinc sulphide may be weighed as such, by igniting in a current of hydrogen. The hydrogen generated in a Kipp's apparatus may contain arsine and hydrogen sulphide, and should be passed through a wash bottle containing a solution of potassium permanganate in concentrated sulphuric acid, then through a flask filled with caustic soda and finally through concentrated sulphuric acid. Explosions may be avoided by placing a small glass tube containing cotton between discs of wire gauze, immediately back of the last drying bottle (Fresenius). Remove the precipitate as completely as possible from the filter, and incinerate the latter on the crucible cover after moistening with a saturated solution of ammonium nitrate. Then place the precipitate and filter-ash in a Rose crucible, mix with a little powdered sulphur, cover, and pass hydrogen from the Kipp's apparatus while gently heating. The crucible should not be heated until all the air has been expelled from the apparatus. Ignite for 5 or 10 minutes, then cool in a current of hydrogen.

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* The addition of ammonium nitrate facilitates the precipitation of zinc sulphide.

† In the quantitative precipitation of zinc by hydrogen sulphide, no free acid other than acetic should be present. The addition of sodium acetate serves to neutralize any liberated mineral acid.

The water of crystallization may be determined by drying a weighed amount of the zinc sulphate at 220° C., to constant weight. The sulphuric acid is determined as given on page 23.

NICKEL SULPHATE.

$NiSO_4$*

The nickel is determined by transforming it into nickelous hydroxide and igniting to nickelous oxide, NiO. The separation of the nickelous hydroxide is best effected by heating about 100 cc. of 10% solution of potassium hydroxide to boiling in a platinum or porcelain dish,† and then adding the nickel solution. Boil for a few minutes more, dilute with water, decant, and wash the precipitate with hot water by decantation. Since the precipitate holds the alkali tenaciously, the ignited nickelous oxide must be repeatedly extracted with hot water.

The sulphuric acid is determined as barium sulphate (see page 23).

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* For the analysis it is best to use the anhydrous salt; the latter is obtained by gently heating the crystallized nickel sulphate, or nickel-ammonium sulphate, in a platinum or porcelain crucible.

† It is not permissible to use glass vessels for the precipitation, since considerable silica and alumina will contaminate the precipitate.

COBALT SULPHATE.

$CoSO_4$*

The cobalt is determined by precipitation with sodium- or potassium hydroxide as given under nickel sulphate. As the ignition of the precipitate gives a mixture of different oxides, it is necessary to reduce the precipitate to metallic cobalt, by igniting in a current of hydrogen. For this purpose use the Rose crucible as described on page 31.

Repeatedly extract the cobalt with hot water to free it from the last trace of alkali, and after drying, reignite in a current of hydrogen.

Second Method :—The cobalt may also be precipitated by Jannasch's method, as follows : Dissolve the salt in 10 cc. of water, add about half its volume of sodium hydroxide, then add 40–50 cc. hydrogen peroxide and warm. Filter, and wash the precipitate with hot water and ignite to metallic cobalt in a current of hydrogen.

As the precipitate is easy to filter and wash, this method is preferable to precipitation as the hydroxide. In all cases, it is advisable to test the metallic cobalt for alkali.

Sulphuric acid is determined as usual.

SEPARATION OF COBALT FROM NICKEL.

First Method :—Precipitation of the cobalt as cobalt-potassium nitrite. Dissolve about 0.4 gram of cobalt-ammonium sulphate and about the same amount of nickel-ammonium sulphate† in 10 cc. of water. Add concentrated potassium or sodium hydroxide in slight excess and then add concentrated acetic acid until the precipitate is redissolved. Add to this solution a freshly prepared, saturated solution of potassium nitrite* which is acidified with acetic acid, and allow to stand for about 24 hours. After standing, test a small amount of the clear solution with more potassium nitrite to see if further precipitation ensues. If necessary, add more of the reagent, allow to stand and repeat the test.

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* For the analysis, use the anhydrous sulphate obtained by gently igniting the crystallized salt.

† The double salts, $NiSO_4.(NH_4)_2SO_4+6H_2O$ and $CoSO_4.(NH_4)_2SO_4+6H_2O$, are easy to obtain, as they crystallize well and do not quickly effloresce.

Filter, and wash with a solution of 1 part potassium acetate and 9 parts water to which has been added a little potasium nitrite acidified with acetic acid. Continue the washing until a portion of the filtrate, after neutralizing with ammonium hydroxide, is not colored brown by 10 times its volume of ammonium sulphide. Dissolve the washed precipitate in concentrated hydrochloric acid, remove the excess of acid by evaporation and precipitate the cobalt with potassium or sodium hydroxide as given in the preceding example.

The nickel may be determined in the filtrate from the cobalt by adding hydrochloric acid and evaporating to dryness ; dissolve the residue in water, add a little hydrochloric acid and precipitate the nickel with potassium or sodium hydroxide. According to Jannasch, the precipitation of nickel is not influenced by the presence of ammonium salts if hydrogen peroxide is added to the sodium hydroxide.

Second Method. Precipitation of the nickel as hydroxide from potassium cyanide solution:—The method consists in transforming both metals into double cyanides, potassium-cobalt cyanide and potassium-nickel cyanide, and then precipitating the nickel as hydroxide $Ni_2(OH)_6$ from the alkaline solution of these compounds. For this purpose, supersaturate the solution with potassium hydroxide, and add pure potassium cyanide until the precipitate redissolves and potassium cyanide is in slight excess. Pass chlorine through the cold solution (previous boiling is not necessary), or add bromine or freshly prepared sodium hypochlorite to the warm solution until all the nickel is precipitated as black hydroxide. Filter, and wash the precipitate with hot water, and reduce to metallic nickel in a current of hydrogen. The nickel must be freed from alkali by digestion with hot water and it should be soluble in hydrochloric acid. Any residue should be tested for silica and alumina.*

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* The potassium nitrite should be tested for alumina, silica and lead. To be independent of these impurities and to obtain an absolutely accurate determination, it is necessary to precipitate the cobalt electrolytically from the solution of the cobalt-potassium nitrite. See note, p. 1.

Add sulphuric acid to the filtrate and evaporate almost to dryness; this changes the colorless potassium-cobalt cyanide into the rose-red sulphate. Dissolve in water, filter from any silica present (dissolved from the vessels), and precipitate the cobalt as given on page 33.

Third Method. Precipitation of nickel from the double cyanide solution by mercuric oxide:—The solution of the double salt is obtained as given in the Second Method, and a little hydrochloric acid is added to form free hydrocyanic acid. The solution is then boiled for some time, replacing the water as it evaporates. The boiling changes the potassium cobaltocyanide into potassium cobalticyanide. Now add pure, washed mercuric oxide, and boil for an hour, which precipitates all the nickel. Filter, wash with hot water, dry, and ignite under the hood to nickelous oxide. The cobalt can be determined in the filtrate as given under the Second Method.

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* As the latter impurities are unavoidable on account of the large amounts of alkali introduced into the solution, it is advisable to determine the nickel electrolytically. See foot-note, page 1.

Fourth Method. Precipitation of the Cobalt with nitroso-β-Naphthol, $C_{10}H_6O(NOH)$*:—This substance with cobalt, forms the compound $[C_{10}H_6O(NO)]_3Co$, cobalti-nitroso-β-naphthol, which is insoluble in hydrochloric acid, whereas the nickel compound, $[C_{10}H_6O(NO)]_2Ni$, is soluble in hydrochloric acid. Add 4-5 cc. hydrochloric acid to the solution of the sulphates of cobalt and nickel, warm, and add a hot solution of nitroso-β-naphthol in 50% acetic acid as long as precipitation ensues. After the precipitate has settled, test to see if the precipitation is complete. Allow to stand for a few hours at the ordinary temperature, filter, and wash first with cold and then with warm 12% hydrochloric acid until all nickel is removed, and then wash with hot water to remove all hydrochloric acid. Dry the precipitate, fold the paper, and ignite in a Rose crucible after adding a little pure, crystallized oxalic acid. To avoid loss, incinerate the filter first at a low temperature, gradually increase the temperature and finally reduce to metallic cobalt in a current of hydrogen, and determine the weight of the metal. (See page 31).

Add sulphuric acid to the filtrate containing the nickel, evaporate the greater part of the acid, and precipitate the nickel as given on page 34.

Since the cobalt precipitate is very voluminous, this method is especially suitable for the determination of a small amount of cobalt in the presence of a large amount of nickel.

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* v. Knorre and Illinski, Ber. deutsch chem. Gesell. 1885, p. 699.

MANGANOUS CHLORIDE.

$MnCl_2+4H_2O$

First Method. Determination of Manganese as Mn_3O_4 :—Dissolve 1. gram of the salt in water in a platinum or porcelain dish, heat almost to boiling and precipitate with an excess of sodium carbonate. Treat the precipitate of manganous carbonate exactly as given in the determination of zinc, page 29. The filtrate still contains a trace of manganese in solution; to separate it, evaporate to dryness in a platinum or porcelain dish, dissolve the residue in hot water and filter off the precipitate on a separate filter. Strongly ignite the two precipitates together with access of air in a platinum crucible over the blast lamp. The manganous carbonate is changed to Mn_3O_4. As the precipitate persistently holds alkali, the ignited residue must be washed with hot water. Decant through a small filter, incinerate the latter and add the ash to the crucible and ignite over the blast lamp to constant weight. According to the author's experience, it is not easy to obtain a constant weight. It is therefore preferable to determine the manganese as the sulphate as recommended by Volhard. For this purpose add to the crucible a little pure, concentrated sulphuric acid, carefully evaporate the excess of acid, and ignite the residue at a moderate heat so that the bottom of the crucible is at a very low red. The precipitate is weighed as $MnSO_4$.

Second Method. Precipitation with ammoniacal hydrogen peroxide. (Jannasch) :—Dissolve the sample in about 100 cc. of water in a porcelain dish, add a mixture of 40–50 cc. of 3% hydrogen peroxide and 10–20 cc. of concentrated ammonium hydroxide. The manganese is precipitated as a dark brown, hydrated peroxide. If the hydrogen peroxide has been added in sufficient excess, the solution will contain small pearly bubbles after stirring. Cover the dish, and heat on the water-bath for 10 or 15 minutes; filter, and wash the precipitate with boiling dilute ammonium hydroxide, and then with pure water, until a portion of the filtrate leaves no residue when evaporated on a platinum foil. Ignite the precipitate and filter in a platinum crucible, which changes it to Mn_3O_4. Compare the preceding method.

Determination of Manganese as Manganous Sulphide:—In some cases, where manganese must be separated, it is necessary to precipitate it as sulphide. Add ammonium chloride or nitrate in slight excess to the solution of the salt, then add ammonium hydroxide to alkaline reaction, heat to boiling and precipitate with ammonium sulphide. The flesh-colored, hydrated manganous sulphide possesses the property of stopping the pores of the filter, and easily passes through the filter on washing, while the anhydrous, green sulphide which is much more dense, may easily be filtered and washed. To precipitate the anhydrous sulphide, add a little potassium oxalate and boil for a few minutes. The addition of ammonium hydroxide and ammonium sulphide to the hot solution, produces at once either the green sulphide or a mixture of the two compounds; complete change into the anhydrous sulphide soon takes place on warming on the sand-bath.*

According to Meineke, the anhydrous sulphide may also be obtained by adding ammonium hydroxide in large excess to the boiling solution, and then precipitating with ammonium sulphide; boil a few minutes and filter. If Meinke's directions are followed, a small amount of manganese passes into the filtrate, owing to decomposition of the ammonium sulphide.

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* Classen, Zeit. f. anal. Chem. Vol. 16, p. 318.

The manganous sulphide mixed with sulphur, must be ignited in a current of hydrogen over the blast, as it may retain sulphur. It is necessary to allow the precipitate to cool in hydrogen, as the warm manganous sulphide is easily oxidized in the air.

The determination is much more simple and accurate if the precipitate is ignited in a platinum crucible, then moistened with concentrated sulphuric acid and gently ignited to the sulphate as given above. The chlorine may be determined by dissolving 0.5–1. gram of the substance in water, and precipitating with silver nitrate as given under Barium Chloride, page 26.

Dry a weighed sample of the salt at 150° C. to constant weight, for the water of crystallization.

POTASSIUM BICHROMATE.

$K_2Cr_2O_7$

Dehydrate the salt by fusing at a gentle heat. Dissolve from 0.5–1. gram of the dehydrated salt in 25–30 cc. of water, add hydrochloric acid and alcohol, and boil until the liquid has assumed an intensely green color. After the alcohol has been expelled, heat to boiling in a platinum or porcelain dish* and add ammonium hydroxide in slight excess. As the chromic hydroxide is somewhat soluble in ammonium hydroxide, heat on the water-bath until the supernatant liquid is perfectly colorless, and the odor of ammonia can no longer be detected. Wash the precipitate by decantation with hot water, and ignite the filter and precipitate to constant weight in a platinum crucible. Weigh as Cr_2O_3.

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* The precipitation should not be made in glass vessels, as ammonium hydroxide, as well as potassium or sodium hydroxide, attacks the glass.

Second Method :—Dissolve a weighed amount of the salt in water, add sodium acetate in excess, acidify with acetic acid and precipitate with neutral lead acetate. The lead chromate is filtered off on a filter which has been dried at 100° C. and weighed, and the precipitate then washed with cold water and dried to constant weight, or what is less to be recommended, it may be gently ignited in a porcelain crucible.

Determination of Potassium :—Evaporate the filtrate from the chromic hydroxide to dryness, in a porcelain or platinum dish, and gently ignite the residue to volatilize the ammonium chloride. Dissolve the salt in the least possible amount of water, filter, and evaporate the filtrate in a weighed platinum dish. The potassium chloride may be dried at 120–130° C. in the air-bath to constant weight, or it may be gently heated in a well closed crucible. Since potassium chloride is volatile at high a temperature, the bottom of the crucible should not be heated above a low red heat.

SODIUM PHOSPHATE.

$Na_2HPO_4+12H_2O$

The determination of phosphoric acid depends upon its separation as ammonium-magnesium phosphate, and ignition of the latter to magnesium pyrophosphate,

$Mg_2P_2O_7$. If exact and concordant results are to be obtained, the precipitation must be made under definite conditions.

Dissolve about 0.5 gram of the air-dried, crystallized salt in 50 cc. of water, add 1/3 the volume of ammonium hydroxide, and then add drop by drop, and with constant stirring, 10 cc. of magnesium chloride solution which contains 101.5 grams of crystallized magnesium chloride,* 200. grams of ammonium chloride and 400. grams of ammonium hydroxide (.96 Sp. Gr.) in a liter. After standing cold† for 2 or 3 hours, filter, and wash‡ with 2 1/2% ammonium hydroxide solution until the filtrate gives no test for chlorine. Dry the precipitate and place it in a porcelain crucible, incinerate the filter on an inverted crucible cover, moisten the precipitate and filter-ash with nitric acid, heat gently for about 5 minutes, then gradually increase the temperature to a full red heat.

If the magnesium pyrophosphate is not pure white, moisten it again with nitric acid and repeat the ignition. A possible reduction of the precipitate on incinerating the filter, may be avoided by dissolving the ammonium-magnesium phosphate off the filter with nitric acid (1.20 Sp. Gr.) and evaporating the filtrate to dryness in a porcelain crucible on the sand-bath. Ignite as given above.

Indirect Determination of Phosphoric Acid :—In all cases where phosphoric acid must be determined in the presence of metals which would be precipitated by ammonium hydroxide, the preceding method cannot be used directly. In such cases, it is necessary to first separate the phosphoric acid as ammonium phospho-molybdate, and from the solution of the latter, to precipitate the phosphoric acid with magnesium chloride. The formation of the ammonium phospho-molybdate, which is insoluble in nitric acid, like the the precipitation of the ammonium-magnesium phosphate, requires the observance of definite conditions.

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* Loges recommends the use of a corresponding amount of the double salt, $MgCl_2 . NH_4Cl + 6H_2O$, which does not deliquesce in the air like the magnesium chloride.

† If the solution is dilute and contains less than .05 gram of phosphoric acid in 100 cc., it should stand for some time to allow a complete separation of the precipitate.

‡ The precipitate is not entirely insoluble in dilute ammonium hydroxide; a filter pump should therefore be used to hasten the washing.

Dissolve about .3 gram of the substance in about 10 cc. of water, and add about 100–150 cc. ammonium molybdate solution.* Sufficient ammonium molybdate should be added so that there is about 1. cc. for 1. milligram of P_2O_5. For complete precipitation of the phosphoric acid, the solution should stand for 1/2 hour at a temperature of 80° C. Filter off the yellow precipitate of ammonium phospho-molybdate and wash it by decantation with dilute (1/3) ammonium molybdate or with ammonium nitrate (20 grams salt in 100 cc. water) which has been acidified with nitric acid.

Dissolve the precipitate in 2 1/2% ammonium hydroxide, then dilute to about 100 cc. with dilute ammonium hydroxide. Add drop by drop, with constant stirring, 10–15 cc. of magnesium chloride solution and proceed as in the direct determination of phosphoric acid.

Determination of Sodium :—For the direct determination of sodium, the phosphoric acid must be removed. Dissolve about 0.5 gram of the salt in water and acidify with hydrochloric acid. Add a sufficient amount of ferric chloride, dilute to 150–200 cc. with water, and add ammonium hydroxide to neutral reaction and boil. The voluminous red precipitate formed is a mixture of ferric hydroxide and ferric phosphate. Filter, and wash by decantation with hot water, until the filtrate gives no test for chlorine. Evaporate the filtrate to dryness in a platinum or porcelain dish and remove ammonium chloride by gently heating the residue. Proceed as given in the Determination of Potassium. See Potassium Bichromate, page 40.

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* The ammonium molybdate solution is prepared by dissolving 150 grams of ammonium molybdate in a liter of water and adding a liter of pure nitric acid of the ordinary concentration. 100 cc. of the solution corresponds to about .1 gram of phosphoric acid.

Determination of Water of Crystallization :—Sodium phosphate loses all its water of crystallization when dried at 300° C. If the anhydrous salt is gently ignited, sodium pyrophosphate is formed.

$$2\ Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

LEAD CHROMATE.

$PbCrO_4$

Finely pulverize the substance, dry at 100°C. and digest about 0.5 gram with fuming hydrochloric acid until completely decomposed; evaporate the excess of acid. This forms lead chloride and chromic chloride. For the complete separation of the former, cool the solution, add an excess of 90–95% alcohol and filter the lead chloride on a filter which has previously been dried at 100°C. and weighed. Wash with alcohol and dry at 100°C. to constant weight.

After expelling the alcohol and hydrochloric acid from the filtrate, the chromium is separated as chromic hydroxide according to the method given under Potassium Bichromate, page 39.

Another method for the separation of lead and chromium depends upon the precipitation of the former as lead sulphide in hydrochloric acid solution. Add hot water to the solution until all the lead chloride is dissolved, and pass a current of hydrogen sulphide.* Filter off the lead sulphide, and wash with water containing hydrogen sulphide. Add a little powdered sulphur and ignite in a current of hydrogen.† Weigh as lead sulphide. See page 31.

The chromium is determined in the filtrate as given above.

SEPARATION OF IODINE FROM CHLORINE.

First method. Precipitation of the Iodine as Palladous Iodide :—Dissolve about .25 gram each of potassium iodide and sodium chloride in water, and slightly acidify with nitric acid. Add palladous nitrate, $Pd(NO_3)_2$, in slight excess. Allow to stand from 24 to 48 hours in a warm place, then filter off the brownish-black precipitate of palladous iodide, PdI_2, on a weighed filter, wash with warm water, and dry at 80°C. to constant weight. Or, the precipitate and filter may be ignited in a Rose crucible until the carbon of the paper is burned off, and then reduced to metallic palladium in a current of hydrogen.

Before the chlorine can be determined as silver chloride in the filtrate, the excess of palladium must be removed. Pass hydrogen sulphide through the warm solution, filter off the palladous sulphide, and destroy the excess of hydrogen sulphide with either chlorine—free hydrogen peroxide or ferric sulphate. After the liquid has stood for some time in a covered dish on the water-bath, filter off the separated sulphur and precipitate the chlorine with silver nitrate as usual.

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* The precipitation of lead as lead sulphide from hydrochloric acid solution is complete only if the liquid is very dilute and the hydrogen sulphide is passed through the solution for a long time.

† Lead sulphide is volatilized on strong ignition. Care must therefore be taken that only the bottom of the crucible is at a low red heat. Classen, Jour. f. prakt. Chem., Vol. 96, p. 257.

Second Method. Precipitation of the Iodine as Thallous Iodide. (Jannasch and Aschoff.):—The separation depends upon the following facts: Thallous Iodide is very slightly soluble in cold water; thallous chloride is slightly soluble in cold water but dissolves much more easily on the addition of certain salts, while these salts at the same time lessen the solubility of the iodide. If alcohol is now added, the iodide is insoluble.

Proceed as follows: Dissolve about 0.5 gram of a mixture of sodium chloride and potassium iodide in about 40–50 cc. water, add 50 cc. of a 20% ammonium sulphate solution and 30 cc. of alcohol. If these conditions are strictly observed, alkaline sulphate is not precipitated with the iodide.

Now add a 4% solution of thallium sulphate until all iodine is precipitated. The thallous iodide, TlI, settles quickly if the solution is gently warmed. Allow to stand for 12 hours at the ordinary temperature, filter on a weighed filter, using suction, wash 2 or 3 times with a mixture of 5 parts ammonium sulphate, 70 parts water and 30 parts alcohol and dry at 100° C. to constant weight.

Expel the alcohol from the filtrate by heating on the water-bath, and dilute to 300 cc. Add silver nitrate, acidify with nitric acid, and heat. Allow the solution to stand hot for some time, so that no silver sulphate will crystallize out, filter off the silver chloride and determine it as given on page 26.

Third Method. Determination by Difference :—Dilute the solution to 100 cc. and divide into 2 equal parts. In one half of the solution precipitate the iodine with palladous chloride as given in the first method, and in the other half, precipitate both halogens together with silver nitrate. Filter off the precipitate in an asbestos tube (page 15), and determine the weight of the silver precipitate. From the weight of the silver precipitate, subtract the amount of silver iodide which corresponds to the weight of the iodine in the palladous iodide, and thus obtain the silver chloride by difference.

SEPARATION OF IODINE FROM BROMINE.

First Method. Precipitation of the Iodine as Palladous Iodide :—Proceed exactly as given in the Separation of Iodine from Chlorine, page 44. The silver bromide obtained is treated like the silver chloride. After the filter has been burned in a porcelain crucible, add a few drops of nitric acid and warm, then add a few drops of bromine water and evaporate to dryness.

Second Method :—Iodine and bromine may be determined by difference in a manner similar to the Separation of Iodine from Chlorine. See Third Method, page 46.

Indirect Determination of Bromine in the presence of Chlorine :—The method depends upon the precipitation of both halogens by silver nitrate and the subsequent conversion of the silver bromide into silver chloride by means of gaseous chlorine. Dissolve about 0.5 gram of a mixture of potassium bromide and sodium chloride in 100 cc.

of water, add silver nitrate, acidify with nitric acid, and warm. Filter off the precipitate in an asbestos tube (page 15), dry at 125–150° C. and weigh. Let P represent the weight of the precipitate.

Close the large end of the tube with a one-hole stopper through which passes a short piece of glass tubing, and clamp firmly in a stand. Pass a current of chlorine* through the tube, loosening the precipitate on the asbestos to facilitate the passage of the gas. Warm the tube gently, and at the same time rotate it on its axis so as to offer as large a surface as possible to the chlorine. Gradually increase the temperature for 15 minutes, avoiding fusion of the precipitate. Repeat this operation until constant weight is obtained. Let p represent the weight of the silver chloride found.

Let x and y represent the weights of silver bromide and silver chloride, respectively, in the mixed precipitate, then,

$$x+y=P \quad - \quad - \quad - \quad (1)$$

After replacing the bromine by chlorine, 143.38 parts by weight of silver chloride are obtained from 187.89 parts by weight of silver bromide; and from x parts by weight of silver bromide, $\frac{143.38}{187.89}$ x, or, .7631x parts by weight of silver chloride, from which the second equation is obtained,

$$0.7631x+y=p \quad - \quad - \quad -(2)$$

By subtraction, (1)–(2), we obtain

$$0.2369x=P-p, \text{ from which,}$$

$$x(AgBr)=\frac{P-p}{0.2369}.$$

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* For analytical purposes, chlorine may be prepared most conveniently by heating potassium bichromate with hydrochloric acid. Pass the gas through a wash bottle containing water, to remove hydrochloric acid and then through a wash bottle containing sulphuric acid, to dry it.

The indirect determination of iodine in the presence of chlorine is made in a similar manner. The calculation is similar, and gives,

$$x(AgI)=\frac{P-p}{0.3893}.$$

If only relatively small amounts of bromine or iodine are present, the results of the indirect method are less exact, because the difference P–p is too small, and therefore the unavoidable error is influenced too much. For the determination of very small amounts of iodine, Jannasch's method, described below, is suitable.

Determination of Chlorine or Bromine in the presence of Iodine, by expelling the latter. (Gooch.) :—This method depends upon the fact that free iodine can be removed, by boiling under conditions which will not volatilize the hydrochloric acid. A very dilute solution of hydrochloric acid can be boiled down to one-fourth of its original volume, without litmus showing a trace of acid in the vapor.

Place about .5 gram each of potassium iodide and sodium chloride or bromide in a flask of at least a liter capacity, and dissolve in 600.–700. cc. of water; add 2.–3. cc. of dilute sulphuric acid and then add a sufficient amount of sodium nitrite. The nitrous acid decomposes the potassium iodide according to the equation:

$$2KI+2HNO_2+2H_2SO_4=I_2+2KHSO_4+2NO+2H_2O.$$

Boil the liquid until the yellow color has disappeared, and reddened litmus paper is not colored lavender blue by the vapors, which will require about ½ hour; the liquid should not concentrate to less than 500. cc.

The chlorine or bromine can now be determined as usual.

If it is desired to determine the iodine, the indirect method may be used. Precipitate the iodine and the other halogen with silver nitrate, and from their weight, subtract the weight of the silver halogen, found after expulsion of the iodine. The difference is the weight of the silver iodide.

Iodine may also be determined indirectly in a mixture containing all three halogens, by expelling the iodine as given above and then determining the weight of the two remaining halogens as silver salts. Subtract the weight of the two silver halides from the weight of the silver chloride, bromide and iodide found in a separate sample, to obtain the weight of the silver iodide. The weight of iodine can easily be calculated from the weight of the silver iodide.

Iodine may also be liberated by ferric sulphate instead of potassium nitrite, according to the equation:

$$2KI + Fe_2(SO_4)_3 = I_2 + 2FeSO_4 + K_2SO_4$$

All reagents used must be free from chlorine.

DIRECT SEPARATION OF IODINE, BROMINE AND CHLORINE.

Jannasch and Aschoff have based a direct determination of iodine upon the principles involved in the preceding method. The iodine is liberated by sodium nitrite and sulphuric acid and distilled over into sodium hydroxide. After the iodine is eliminated, the bromine is liberated by potassium permanganate and acetic acid, and similarly distilled and absorbed by sodium hydroxide. The separated halogens may then be determined in the usual manner.

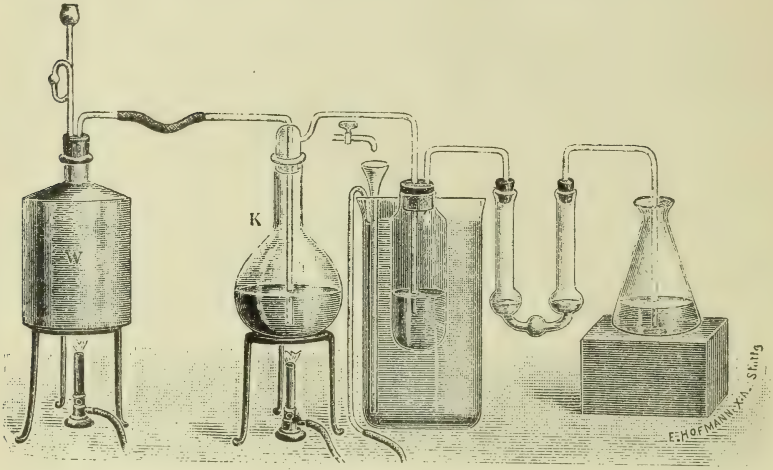

Fig. 17.

1. Determination of Iodine :—A strong-walled flask K, Fig. 17, with a ground glass stopper, is used for the distillation. A tube for the introduction of steam, reaching nearly to the bottom of the flask, and a tube for carrying the iodine vapor over into the sodium hydroxide solution, are fused into the stopper. The tube carrying the iodine vapor should have the form shown in the figure, to prevent the solution being carried over. A deep cylindrical flask, of at least 500 cc. capacity, is used to hold the sodium hydroxide solution ; to avoid any loss of iodine which might be carried over mechanically, a Peligot tube and an Erlenmeyer flask are connected with the main absorption flask. The latter should be cooled during the distillation, preferably in a breaker, so that the reaction may be observed. W is an apparatus in which steam may be generated.

Place a mixture of about .250–.300 gram each of sodium chloride, potassium bromide and potassium iodide in the distilling flask and dissolve in about 750 cc. of water. Add 5. cc of dilute sulphuric acid and then 1 gram of sodium nitrite in 10. cc. of water and stopper at once. Connect with the absorption flask, which should contain 50. cc. of pure sodium hydroxide in 50. cc. of hydrogen peroxide; the Peligot tube should contain a suitable amount of the same mixture, and the Erlenmeyer flask, 25–50 cc. of very dilute, sodium peroxide solution.

Now pass a current of steam into the flask; the iodine vapor at first condenses in the cold tube, but it is soon carried over into the sodium hydroxide solution, where oxygen is liberated in considerable quantity. The reaction is as follows:

$$6NaOH+6I=5NaI+NaIO_3+3H_2O.$$

Since the presence of iodate interferes with the precipitation of iodide by silver nitrate, hydrogen peroxide is added to the sodium hydroxide, which reduces the iodate to iodide, with liberation of oxygen:

$$NaIO_3+3H_2O_2=NaI+3H_2O+6O.$$

After distilling for about 15 minutes, the solution in the distilling flask will be completely decolorized, showing the complete removal of the iodine. To prevent the sodium hydroxide from sucking back, the current of steam should not be stopped until the exit tube has been removed from the absorption flask. Rinse off the tube with water, transfer the contents of the two absorption flasks to a porcelain dish and add 50 cc. of hydrogen peroxide to oxidize any traces of sodium nitrite; cover the dish, and warm for some time on the water-bath. Stir, and add a solution of silver nitrate until a permanent brown precipitate of silver hydroxide is formed; the iodine gradually decomposes the silver hydroxide, forming yellow silver iodide, and the permanent brown silver hydroxide shows that sufficient silver nitrate has been added to change the sodium iodide into silver iodide. Acidify with nitric acid, warm on the water-bath until the precipitate has settled, filter while hot, and determine like silver chloride, page 26. The solution should not be allowed to cool, as the precipitate may be contaminated with silver nitrate, which is difficult to wash out.

2. Determination of Bromine :—Add sodium hydroxide to the contents of the distilling flask, to weakly alkaline reaction, to prevent volatilization of hydrochloric or hydrobromic acid, and concentrate to 500 cc. It is advisable to use a flask of about ¾–1 liter capacity. Cool the solution, and add 60 cc. of dilute acetic* acid (1–2), and then a concentrated solution of 1–1½ grams of potassium permanganate. Connect the apparatus as in the distillation of iodine, and pass a current of steam. The liquid gradually becomes cloudy by separated manganese dioxide, and after distilling 45–75 minutes, the bromine will be expelled. The disappearance of bromine vapors is not a certain indication that the bromine has all been expelled, as traces are held in the solution for a long time. The current of steam should not be too rapid, as the bromine might not all be absorbed by the sodium hydroxide.

After distillation, treat the contents of the absorption flasks as given under the determination of iodine, and then precipitate the bromine with a mixture of 10% silver nitrate and an equal volume of nitric acid; warm on the water-bath for ½ hour, filter while hot, and determine the bromine as given for chlorine.

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* It is of the greatest importance to use chemically pure acetic acid. If the latter contains any caproic acid or purpurol, etc., the bromine may be .5 per cent too low, owing to action on these bodies.

3. Determination of Chlorine:—Destroy the potassium permanganate in the liquid remaining in the distilling flask, by warming a short time with sodium hydroxide and a little alcohol. Filter, and wash with luke-warm water. If hot water is used, the finely divided precipitate may run through the filter. The latter difficulty may be avoided by washing with a 1% solution of chlorine—free sodium nitrate. Precipitate the chlorine as usual, in the clear filtrate.

DOLOMITE.

Constituents: Calcium and Magnesium Carbonates, generally with small amounts of Ferrous Carbonate, Alumina and Silica.

First Method:—Finely pulverize the substance, and dry at 100° C. Dissolve from 1–1.5 grams in hydrochloric acid in a covered porcelain dish, warm on the water-bath until no more carbon dioxide is evolved, and then evaporate to dryness, Heat the dry residue for some time at 120° C. in the air-bath, for the complete dehydration of the silicic acid. After cooling, moisten with hydrochloric acid, warm for a few minutes on the sand-bath, and then dilute with water. Filter off the silica, wash it with hot water, ignite in a platinum crucible and weigh. Add hydrogen peroxide or nitric acid to the filtrate to oxidize ferrous iron, warm, add ammonium chloride in excess*, stir, and add ammonium hydroxide to weakly alkaline reaction. Filter off the precipitate of ferric- and aluminum hydroxides as rapidly as possible, avoiding exposure to the air, wash with hot water, dissolve off the filter with warm dilute hydrochloric acid and reprecipitate with ammonium hydroxide.* Ordinarily, the precipitate is so small that the iron and alumina are not separated. If it is desired to separate them, proceed as given under Red Hematite.

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* The addition of the ammonium chloride prevents the precipitation of magnesium hydroxide.

Precipitate the calcium in the filtrate from the iron and aluminum hydroxides, with an excess of ammonium oxalate. The calcium may be weighed either as carbonate or oxide; see page 21. As the calcium oxalate always contains some magnesium oxalate, in exact analysis the precipitate must be dissolved in hydrochloric acid and the precipitation repeated. Decant the clear supernatant liquid through the filter, dissolve the calcium oxalate in the breaker with warm hydrochloric acid, dilute with water, first add a little ammonium oxalate and then ammonium hydroxide in slight excess. Unite the two filtrates,† concentrate by evaporation, cool, and precipitate the magnesium with sodium phosphate. The further treatment of the precipitate is given on page 27.

Second Method:—The calcium, magnesium, etc., may be determined according to a method previously recommended by the author‡. Separate the silica as given above, and evaporate the filtrate to dryness. Oxidize the iron with hydrogen peroxide or bromine water, warm, and add 2 or 3 times as much neutral potassium oxalate (1–3 parts water) as was taken of the substance for analysis. If the separated calcium oxalate is not pure white, add more hydrogen peroxide or bromine water, and digest for a short time on the water-bath. Filter off the calcium oxalate, wash with hot water containing a little ammonium oxalate, and concentrate the filtrate by evaporation, to about 25 cc. Heat to boiling, and add an equal volume of concentrated acetic acid. The magnesium is separated as oxalate, and is washed and ignited to magnesium oxide, as given on page 28. After evaporating off the alcohol and acetic acid, precipitate the iron and alumina in the filtrate with ammonium hydroxide. For complete precipitation, digest on the water-bath or sand-bath until the supernatant liquid appears perfectly clear.

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* The double precipitation is necessary, as the first precipitate always contains a small amount of calcium and magnesium.

† Occasionally, on long standing, crystallized magnesium oxalate separates in the filtrate from the calcium oxalate; if this is the case, acidify with hydrochloric acid, warm the solution, add ammonium hydroxide and precipitate the magnesium as given above.

‡ Zeit. f. anal. Chem. Vol. 18, p. 373.

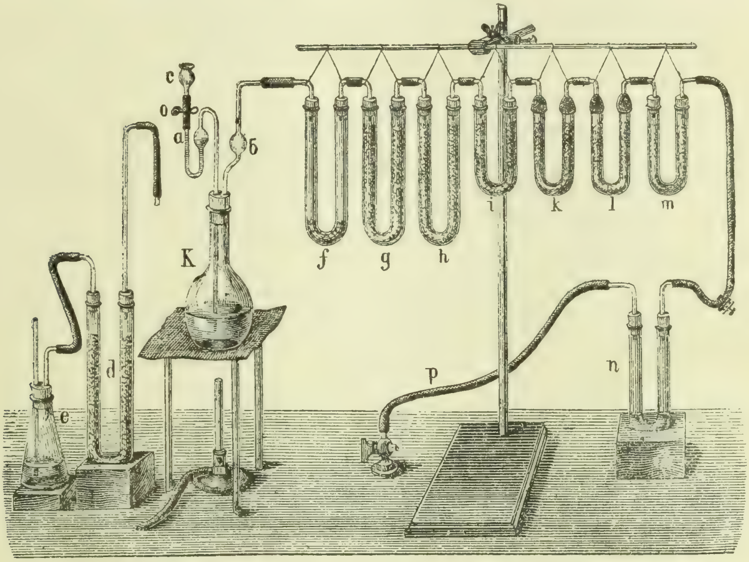

Fig. 18.

The carbon dioxide is determined in the apparatus originally devised by Kolbe and modified by Fresenius, or the more simple apparatus, devised by the author,* depending upon the absorption of carbon dioxide by soda lime† may be used.

The apparatus devised by Fresenius, Fig. 18, is composed of the following parts. The flask K for the decomposition of the substance, of 200–300 cc. capacity, is closed with a two-hole rubber stopper. Through one hole, passes the safety tube a, through the other hole, a bulb tube b. The safety tube is joined at a with a funnel by means of a piece of rubber tubing, so that the addition of acid may be regulated by the pinchcock o. The soda-lime tube d, and the flask e, containing the potassium hydroxide, may then be connected after the substance is in solution. The bulb tube b, which condenses the steam, is cut off at an angle at its lower end.

The carbon dioxide is first passed through two U-tubes, each about 17 cm. long and 16 mm. wide, to separate the carbon dioxide from water vapor and hydrochloric acid.

The first tube, f, is filled in its lower portion with calcium chloride, the second tube, g, is completely filled with pieces of calcium chloride. To absorb the hydrochloric acid, the tube h is filled with small pieces of pumice which have been boiled in a concentrated solution of copper sulphate, and then dried in the air bath at 250–300°C. A calcium chloride tube, i, is connected with h. Two U-tubes, each 11 cm. long and 12 mm. in diameter, 5/6 filled with coarse soda-lime, and the remainder with small pieces of calcium chloride, are used to absorb the carbon dioxide. To prevent backward diffusion of carbon dioxide or water vapor into the train, the tube m, of the same dimensions as the absorption tube, is filled with calcium chloride on the side next to the apparatus, and with soda lime on the other side. The bend of the tube n, is filled with water so that the rate of the reaction may be observed.

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* Zeit. f. anal. Chem., Vol. 15, p. 221.

† For the determination of carbon dioxide by difference, see analysis of Soda.

It should be remembered that calcium chloride may absorb carbon dioxide; therefore it should be saturated with the gas before being used.

After the two absorption tubes k and l, have been weighed*, 2–3 grams of the substance have been put in the decomposing flask, first test to see that the apparatus is tight. Connect all the parts, close the pinch-cock o and evacuate by suction on the tube p; if the connections are all tight, air will bubble through the tube n for only a short time.

Now open the pinch-cock o, pour some water into the flask, again close the pinch-cock and fill the funnel with dilute hydrochloric acid. Slowly add the acid to the flask by gradually opening the pinch-cock. When action has ceased, remove the funnel c, connect the tube d with the funnel tube a, and aspirate a slow current of air through the apparatus; at the same time heat the flask until the liquid boils. The current of air sweeps all the carbon dioxide into the absorption tubes, and heating the liquid expels the absorbed carbon dioxide. When the apparatus is completely cold weigh the tubes k and l; the gain in weight is the amount of carbon dioxide present.

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* To prevent these absorbing moisture while being weighed, they should be capped with small pieces of rubber tubing closed at one end with a piece of glass rod.

The arrangement of the apparatus devised by the author is shown in Fig. 19.

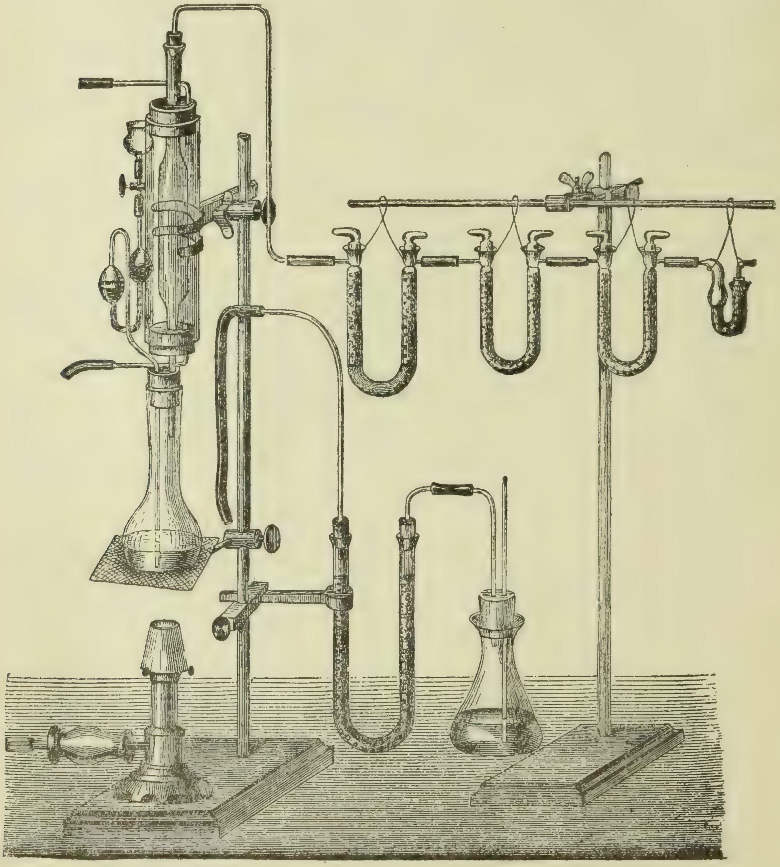

Fig. 19.

A tube of 2 1/2–3 cm. in diameter, with a tube of 1 1/2 cm. diameter fused on the upper end, and one of 6–7 mm. fused on the lower end, is used for the condensation of steam and hydrochloric acid. The tube is surrounded by a wider tube about 23 cm. in length, and 4 cm. in width. If the inner tube is cooled in the usual manner, the dilute hydrochloric acid may be boiled for hours without a trace of acid being recognizable in the upper end of the condenser. The carbon dioxide is dried by passing through a tube filled with glass beads moistened with concentrated sulphuric acid. The bend of the tube is filled with acid so that the rate of evolution of the gas can be observed. Such a tube can be used for a whole series of experiments without renewing the acid. The carbon dioxide is absorbed by soda-lime. To protect the two tubes filled with soda-lime, a small tube filled with small pieces of potassium hydroxide may be used, although the author has not found it necessary.

A still simpler form of apparatus, Fig. 20, is recommended by Friedheim. The condenser is replaced by a tube inclined at an angle. The horizontal part of the tube is filled with calcium chloride and is used as a substitute for the U-tubes. A Geissler's apparatus is used to absorb

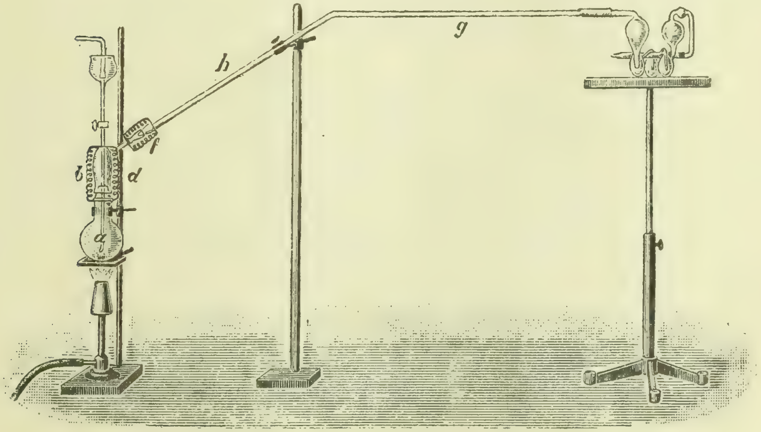

Fig. 20.

the carbon dioxide; the only advantage it has over the soda-lime tube is that the course of the reaction may be observed.

All parts of the apparatus are connected by ground-glass joints, and only the potash apparatus is connected with rubber tubing. The cap b is ground onto the neck of a 150 cc. flask, and the two parts are held together by a spiral spring d. Through the cap, and fused into it, passes the funnel tube with a glass cock. The lower end of the funnel tube is bent upwards. The tube e is also ground into the funnel. The bent drying tube h g, is joined to the side of the cap by a ground glass joint, and is likewise held in place by springs. The drying tube has a diameter of about 10 mm. and the length of each arm is about 30 cm; the horizontal part is drawn out so that it may easily be connected with the absorption apparatus.

Pieces of calcium chloride of about the size of peas should be used, and they should be freed from fine powder by sifting. To fill the tube, place some glass wool in the lower end of the inclined arm h, unite the upper end with the air pump and exhaust, closing the open end with the finger.

By quickly removing the finger, the glass wool is sucked over to the narrow end of the tube, The tube is filled with calcium chloride to within about 6 cm. of the angle, another wad of glass wool is then sucked in as described, to hold the calcium chloride in place, and the arm h is then carefully cleaned of any adhering calcium chloride.

The absorption apparatus is filled with potassium hydroxide of Sp. Gr. 1.23, (1 part potassium hydroxide : 2

parts water) so that each bulb is about two-thirds full. The horizontal tube is filled with pieces of potassium hydroxide and calcium chloride. During the operation, the exit end of the absorption apparatus is joined to the tube filled with pieces of caustic potash, which need not be weighed.

When the apparatus is ready, a quantity of the substance, weighed by difference, is placed in the flask, water is added up to the lower end of the funnel tube, and the train then tested to see if the connections are tight.

The substance is decomposed by acid as given on page 57. The boiling must be conducted so that the steam is condensed about one-half the way up the inclined tube. The potash apparatus is weighed after standing in the balance case from one-half to three-quarters of an hour.

If the dolomite that has been dried at 100° C. loses more water on ignition, the latter cannot be determined by loss on gentle ignition, as carbon dioxide may be expelled, and any ferrous iron present may be oxidized. In this case water may be determined by direct weighing. Ignite the substance in a closed tube of difficultly-fusible glass, about 38 cm. long and 1 cm. in diameter.

Fill the tube one-third full with lead carbonate that has previously been gently ignited. Add the dolomite or calcite mixed with some lead carbonate, fill the remainder with lead carbonate, and close loosely with ignited asbestos. After a canal has been formed in the tube by tapping on the table, it is closed with a dry rubber or cork stopper, and connected with a previously weighed calcium chloride tube. Place the tube in a combustion furnace and heat the lead carbonate at the closed end first, then gradually heat the tube its entire length.

If water condenses in the tube outside of the furnace, it may be driven over into the calcium chloride tube by gently heating the tube with a small flame. After decomposition, reweigh the calcium chloride tube.

BARITE.

Constituents: Barium Sulphate, commonly with a small amount of Strontium Sulphate.

Intimately mix about 1 gram of the finely pulverized mineral, dried at 100° C., with about 4 or 5 times its weight of sodium carbonate* and fuse in a platinum crucible over the blast lamp. Continue the heating until the mass is in quiet fusion, and then pour the contents of the crucible into a platinum dish. If the latter is sufficiently large, place the crucible also in it, add water, and digest on the water-bath until no hard particles can be felt with a glass rod. If it is not desired to pour out the contents†, allow the crucible to cool, place it in a large porcelain dish and digest with warm water. This will require more time than if a platinum dish is used. The solution contains all the sulphuric acid as sodium sulphate, besides undecomposed sodium carbonate; the residue consists of barium and strontium carbonates. After rinsing off the crucible with water, filter, and wash the precipitate until a drop of the filtrate gives no reaction for sulphuric acid.

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* This is prepared by gently heating sodium bicarbonate, which can be had in commerce chemically pure. If a blast lamp is not at hand, the more easily fusible mixture of 5 parts sodium carbonate and 7 parts potassium carbonate, may be used for the decomposition.

† Stockmann, Zeit. f. anal. Chem. Vol. 15, p. 283, recommends allowing the crucible to cool and then reheating until the mass begins to fuse around the edges. Allow to cool again, and add water enough to cover the contents of the crucible. On warming with a small flame, the fused mass may easily be removed from the crucible.

Gently ignite the precipitate in a crucible and weigh as barium and strontium carbonates. For the separation of barium and strontium, see Index.

The sulphuric acid may be determined in the filtrate. Carefully add hydrochloric acid as long as effervescence takes place, warm until until no more carbon dioxide is evolved, and precipitate with barium chloride. See page 23. If the barite contains silica, it will pass into the filtrate with the sodium sulphate, and must be separated before the sulphuric acid can be determined. In this case, add hydrochloric acid and evaporate to dryness in a platinum or porcelain dish. Heat for some time in an air-bath at 120° C,, cool, moisten with hydrochloric acid and dissolve in water. See page 53. The filtrate from the silica is used for the determination of the sulphuric acid. The silica is determined as given above, under Dolomite.

If the barite contains calcium sulphate, see Index for the separation of the three sulphates.

ALLOY OF COPPER AND ZINC (IRON, NICKEL AND LEAD).

BRASS.

Dissolve about .2–.3 gram of the alloy in dilute nitric acid, in a small, covered porcelain dish, warm on the water-bath, and finally evaporate to dryness. If lead is present, add a little dilute sulphuric acid, and heat until all nitric acid is expelled. Add cold water, and stir with a glas rod until the lead sulphate appears pure white, and then add one-third the volume of alcohol. Filter, and wash with dilute alcohol until the sulphuric acid is all removed, dry, and ignite in a porcelain crucible. The incineration of the filter reduces any adhering lead sulphate to metallic lead; therefore proceed as given under silver chloride, page 26, by burning the filter on the inverted crucible cover. Dissolve the metallic lead in a few drops of nitric acid, add a drop or two of pure sulphuric acid, carefully evaporate to dryness, and then ignite until no more fumes of sulphuric acid are evolved. The residue is lead sulphate.

Completely remove the alcohol in the filtrate by evaporation on the water-bath, and separate the copper from the zinc by hydrogen sulphide. To avoid the separation of zinc sulphide with the copper sulphide, add 20 cc. of dilute hydrochloric acid, heat to boiling and pass hydrogen sulphide until the liquid is cold. Filter off the copper sulphide, wash first with hydrochloric acid, Sp. Gr. 1.05, saturated with hydrogen sulphide, and then with hydrogen sulphide water, to completely remove the hydrochloric acid.*

Ignite the copper sulphide in a Rose crucible in a current of hydrogen, and weigh as cuprous sulphide, Cu_2S. See page 31.

The zinc may be precipitated in the filtrate from the copper sulphide, either as zinc sulphide or zinc oxalate. For the first method, remove the excess of hydrochloric acid by evaporation, dilute with water, add an excess of sodium acetate and a few drops of acetic acid, and precipitate the zinc as zinc sulphide, by passing hydrogen sulphide. See page 30.

If the zinc is to be separated as the oxalate and determined as the oxide, the hydrochloric acid as well as the sulphuric acid, must be removed. Evaporate to dryness on the water-bath, then heat on the sand-bath until no more fumes of sulphuric acid are evolved. Dissolve the cooled residue in water, and proceed as given on page 30.

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* According to Berglund, a mixture of 20 volumes of hydrogen sulphide water and 1 volume of hydrochloric acid, (Sp. Gr. 1.10), may be used as a washing solution.

The latter method is more rapid than the former, as the filtration of zinc sulphide is very tedious and requires much attention.

If the brass contains iron, it must be removed before precipitating the zinc, if the first method is followed. In that case, concentrate the filtrate from the copper sulphide to remove the hydrochloric acid and hydrogen sulphide, oxidize with bromine water, and precipitate the iron with ammonium hydroxide. Filter, wash the precipitate, dissolve it in hydrochloric acid and reprecipitate with ammonium hydroxide to remove the zinc.

If the brass contains nickel, its separation from zinc by the method given under German Silver is not suitable, since according to the experiments of Beilstein*, this method does not give accurate results, if a small amount of nickel is to be separated from a large amount of zinc. To separate the two metals, proceed as follows: Add ammonium hydroxide to the sulphuric or nitric acid solution of the metals until alkaline, and then acidify with pure citric acid. Dilute with cold water so that there is about 1 gram of the substance in 1 liter, and then pass hydrogen sulphide for about 5–10 minutes. Hydrogen sulphide should not be passed for a longer time, as some of the nickel may be precipitated with the zinc. If sufficient hydrogen sulphide has been passed, the solution should smell appreciably of the gas, after standing for half an hour. After the solution has stood cold for 24 hours, filter off the zinc sulphide, wash with hydrogen sulphide water to which has been added a little ammonium nitrate. Weigh as zinc sulphide. See page 31.

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* Ber. deutsch, chem. Gesell, Vol. 11, p. 1715.

Concentrate the filtrate by evaporation and separate the nickel as nickelous hydroxide. See page 32.

ALLOY OF COPPER AND SILVER.

SILVER COINS.

Dissolve about 0.5 gram of the silver coin in dilute nitric acid, in a covered porcelain dish. Warm on the water-bath until in complete solution, and finally evaporate to dryness. Dissolve the residue in hot water, transfer to a beaker, and precipitate the silver by adding dilute hydrochloric acid drop by drop. On warming and agitating the solution, the silver chloride collects together and can then be filtered. The further treatment of the precipitate is given under Barium Chloride, page 26.

Precipitate the copper in the filtrate as cuprous sulphide, by passing hydrogen sulphide. Heat the solution to boiling, and pass the gas until the solution is cold; filter off the precipitate as quickly as possible, avoiding exposure to the air by covering the beaker and funnel with watch glasses. Wash with hydrogen sulphide water, dry, add a little sulphur, and ignite strongly in a current of hydrogen. See page 31. Weigh as cuprous sulphide, Cu_2S. As the cuprous sulphide oxidizes very easily, the filtration and washing of the precipitate should not be interrupted. If any oxidation does take place, shown by the cloudiness of the filtrate, wash the precipitate on the filter with hydrogen sulphide water, again pass hydrogen sulphide through the filtrate, and filter off the small amount of cuprous sulphide on a special filter.

ALLOY OF COPPER, TIN AND ZINC (IRON).

BRONZE COINS.

If an alloy containing tin as one of its principal ingredients, is dissolved in concentrated nitric acid, pure stannic oxide is not obtained, but it is contaminated with copper oxide, etc. If, however, nitric acid of a definite concentration is used to dissolve the alloy, pure stannic oxide remains insoluble* Dissolve from 0.5–1 gram of the alloy in 6 cc. of nitric acid, (1.5 Sp. Gr.) in a covered porcelain dish, and gradually add 3 cc. of water. When in solution, dilute with 50 cc. of hot water, filter after the stannic oxide has settled, wash the precipitate with hot water, and determine its weight. For this purpose, dry the precipitate, remove as much as possible from the filter, and transfer to a porcelain crucible. Incinerate the filter on an inverted crucible cover. Moisten the ash with a few drops of nitric acid to oxidize the reduced tin, and carefully warm. Transfer to the crucible, cover, and ignite strongly over the blast lamp.

Add about 2 grams of concentrated sulphuric acid to the filtrate from the stannic oxide, and evaporate on the water-bath to remove the nitric acid. Dissolve the residue in water, and determine the copper as sulphocyanate, as given on page 23.

To determine the iron and zinc in the filtrate from the copper, destroy the excess of potassium sulphocyanate by evaporation with nitric acid, and separate the iron from the zinc by two precipitations with ammonium hydroxide. Determine the iron as given on page 24, and precipitate the zinc as zinc sulphide from acetic acid solution, as given on page 31.

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* Busse, Zeit. f. anal. Chem., Vol. 17, p. 53.

ALLOY OF TIN AND LEAD.

SOFT SOLDER.

Separate the tin and lead exactly as given above. To determine the lead, add dilute sulphuric acid to the filtrate from the tin, and evaporate on the water-bath until all the water is removed. Cool, add alcohol, and treat the lead sulphate as given in the method on page 63.

ALLOY OF NICKEL AND COPPER.

NICKEL COINS.

Dissolve the alloy in nitric acid, and evaporate to dryness on the water-bath, Dissolve the residue in water, acidify with hydrochloric acid, and precipitate the copper as cuprous sulphide, by passing hydrogen sulphide through the hot solution. Filter, wash, ignite, and weigh the precipitate, with the precautions given under Brass, page 64. Expel the hydrogen sulphide from the filtrate by heating, and precipitate the nickel as nickelous hydroxide. This method requires the absence of hydrochloric acid.

According to Busse*, copper cannot be completely separated from nickel by a single precipitation with hydrogen sulphide. Since it is necessary to dissolve the copper sulphide and repeat the precipitation, it is preferable to separate the copper as sulphocyanate. Dissolve from 0.5–0.8 gram of the alloy in nitric acid, 1.18 Sp. Gr., add 1 cc. of concentrated sulphuric acid, and evaporate on the water-bath. Dissolve the residue in a little water, and add 50 cc. sulphurous acid and 2 grams potassium sulphocyanate. After standing for 12 hours, filter, and treat the precipitate as given on page 23. Add 10 cc. of nitric acid to the filtrate and evaporate to dryness. Dissolve the residue in a little water and precipitate the nickel as given on page 32.

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* Zeit. f. anal. Chem., Vol. 17, p. 60.

If the nickel is precipitated as nickelous hydroxide, any zinc which may be present in the alloy will pass into the filtrate. To determine the zinc, acidify the solution with acetic acid, and precipitate it as sulphide. See page 30.

Besides the metals mentioned above, nickel coins often contain an appreciable amount of iron and cobalt. In the precipitation of the nickel as nickelous hydroxide, iron and cobalt are also precipitated. In this case, it is convenient to reduce the precipitate to the metallic state in a current of hydrogen, and then determine the weight of the nickel + cobalt + iron. Dissolve the metals in nitric acid, nearly neutralize with ammonium hydroxide and then add an excess of ammonium carbonate. After the solution has stood warm for some time, filter off the precipitate of ferric hydroxide, dissolve it off the filter with hydrochloric acid, and reprecipitate with ammonium carbonate. Reduce to metallic iron by ignition in a current of hydrogen. To determine the cobalt, evaporate the filtrate from the ferric hydroxide to dryness, remove the ammonium salts by gentle ignition, and dissolve the residue in hydrochloric acid with a few drops of nitric acid. Remove the acid by evaporation, and precipitate the cobalt as potassium-cobalt nitrite, as given on page 33.

Subtract the weight of the metallic iron + cobalt, from the weight of the three metals, to obtain the weight of the nickel.

ALLOY OF LEAD AND ZINC.

Dissolve the alloy in nitric acid, add a little dilute sulphuric acid, and concentrate on the water-bath until all nitric acid is expelled; dissolve the residue in water, and add a third of its volume of alcohol. Filter off the lead sulphate, wash with dilute alcohol, dry, ignite and weigh. See page 63.

Expel the alcohol from the filtrate, and determine the zinc either as sulphide or as oxide.

The two metals may also be separated by hydrogen sulphide. In this case, evaporate the nitric acid solution to dryness, dissolve the residue in considerable water, add a few drops of hydrochloric acid, and precipitate the lead with hydrogen sulphide. See page 44.

Precipitate the zinc as sulphide, carbonate, or oxalate, in the filtrate from the lead. See page 30.

ALLOY OF BISMUTH AND COPPER.

Dissolve the alloy in nitric acid, and evaporate to dryness on the water-bath. Add a few drops of hydrochloric acid to the residue, and dilute with considerable water. When the bismuth oxychloride has settled, and the liquid remains clear on adding more water, filter off the precipitate on a dried and weighed filter, wash with water containing a few drops of hydrochloric acid, and dry the precipitate of bismuth oxychloride, $BiOCl$, at 100° C., to constant weight.

Determine the copper in the filtrate from the bismuth, as oxide or sulphide. Copper may also be separated in the metallic state.

For the latter method, concentrate the filtrate in a weighed platinum dish*, and place a small piece of zinc or cadmium in the liquid. If necessary, add sufficient hydrochloric acid to produce a slow generation of hydrogen, and cover the dish with a watch glass. Allow the reduction† to continue until ammonium hydroxide shows the absence of copper on testing a portion of the clear liquid. Decant through a small filter and wash the copper with hot water by decantation until the hydrochloric acid is all removed. Finally remove the water by rinsing the dish with alcohol. Dry the copper at 100° C. to constant weight.

ALLOY OF LEAD AND BISMUTH.

Dissolve the alloy in nitric acid, evaporate on the water-bath to the consistency of syrup, add a little water, stir with a glass rod and again evaporate. Repeat this treatment three or four times and finally evaporate to dryness.

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* A porcelain dish may be used, but the reduction is much slower.

† Cadmium is preferable to zinc, as the latter ordinarily leaves a residue of lead on solution in acids. As cadmium is attacked less than zinc by dilute acids, the same piece may be used for several reductions. Classen, Jour. f. prakt. Chem., Vol. 96, p. 257.

There should be no odor of nitric acid in the residue. To the cooled mass add a cold solution of one part ammonium nitrate to 500 of water and allow to stand for a short time. Filter off the basic bismuth nitrate, wash with ammonium nitrate solution of the above concentration, dry and ignite in a porcelain crucible. The filter should be incinerated on the inverted crucible cover. Weigh as Bi_2O_3.

As a check, the bismuth oxide may be reduced to metallic bismuth by gentle ignition in a current of hydrogen. Precipitate the lead as sulphide, in the filtrate from the bismuth, either by hydrogen sulphide or ammonium sulphide, and determine it as such, according to the method given on page 44.

Another method of separating the two metals, depends upon the insolubility of lead sulphate, but it is less simple than the above method. Evaporate the solution of the alloy, to expel the nitric acid, and then add hydrochloric acid until the bismuth is all dissolved.* The amount of acid to be added may be found by placing a little of the solution on a watch glass, and adding a few drops of water; if the solution becomes milky, more acid must be added. Rinse the solution on the watch glass back into the dish with alcohol. Add dilute sulphuric acid to precipitate the lead, and if some lead chloride has separated, allow the solution to stand for some time. When all the lead is in the form of sulphate, add alcohol (Sp. Gr. .80). Filter off the lead sulphate, wash first with alcohol containing a little hydrochloric acid, and finally with pure alcohol. Treat the precipitate as given on page 63.

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* If the alloy contains considerable lead, some lead chloride may crystallize out at this point.

Separate the bismuth as bismuth oxychloride, $BiOCl$, in the filtrate from the lead sulphate, by the addition of an excess of water. When all the bismuth is precipitated, which may be ascertained by adding more water, filter, and reduce to metallic bismuth by fusion with potassium cyanide*. For this purpose, ignite the precipitate in a porcelain crucible, cool, and add 5 times the amount of potassium cyanide, and fuse over the blast lamp. By continued heating, the small molten globules of bismuth can be united into one large globule. After cooling, extract the fuse with water, and filter on a dried and weighed filter. Wash first with dilute and then with strong alcohol. After drying the bismuth at 100° C., cool and weigh.

When the bismuth is fused with potassium cyanide in a porcelain crucible, the latter is often more or less attacked, and the reduced bismuth is contaminated with the material of the crucible. This error can be avoided by dissolving the bismuth in dilute nitric acid, and weighing the residul matter from the crucible.

ALLOY OF COPPER, ZINC AND NICKEL.

GERMAN SILVER.

The copper may be separated from the other metals by precipitation as sulphocyanate, according to the method given under Nickel Coins, page 68.

Add about 10 cc. of nitric acid to the filtrate from the copper sulphocyanate, evaporate to dryness on the water-bath, add a little hydrochloric acid, and dissolve in water. Dilute the solution so that there is about 1 gram of zinc in 500 cc. of solution. Neutralize with sodium carbonate so that there is only a slight amount of free acid present. This is best done by adding sodium carbonate until a precipitate is formed, and then dissolving the latter with a little dilute hydrochloric acid. Pass hydrogen sulphide into the cold solution as long as zinc sulphide is precipitated. Then add a few drops of a dilute solution of sodium acetate, to neutralize the free hydrochloric acid. Continue the introduction of hydrogen sulphide until the liquid smells strongly of the gas. After standing 12 hours, filter and wash the zinc sulphide with water to which a little ammonium nitrate has been added, and determine the zinc as given on page 31. After expelling the hydrogen sulphide from the filtrate, the nickel may be precipitated and determined as given on page 34. If the above conditions are strictly observed, the zinc sulphide will be free from nickel sulphide. Without considerable skill and experience it is difficult to effect an exact separation of the two metals with one precipitation. The zinc sulphide should therefore be dissolved, and the precipitation repeated, to remove the nickel sulphide.

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* In this case, the bismuth oxychloride cannot be weighed directly, as in the presence of sulphuric or phosphoric acids, the bismuth forms compounds with these acids.

According to Hampe, it is preferable to precipitate the sulphides from formic acid solution. Add from 15–20 cc. of formic acid to every 250–500 cc. of the solution. Render the solution alkaline with ammonium hydroxide, add the formic acid, and pass hydrogen sulphide through the hot solution. Filter, and wash the precipitate with hydrogen sulphide water to which has been added a little ammonium formate and formic acid.

V. Berg obtained better results with Hampe's method, by the addition of only 3 cc. of formic acid to about 350 cc. of the solution. The precipitate should be filtered at once after passing the hydrogen sulphide, as nickel may be precipitated if the solution is allowed to stand too long.

The two metals may also be separated in the following manner :—After freeing the solution from potassium sulphocyanate by evaporation with nitric acid, precipitate the nickel as nickelous hydroxide according to the method given on page 32. Filter, and wash the precipitate with hot water. As the precipitate may still contain a small amount of zinc, it should be dissolved, and the precipitation repeated.

Unite the filtrates, acidify with acetic acid, and precipitate the zinc by passing hydrogen sulphide through the boiling solution. If cobalt or iron are present, the nickel must be separated from these metals. Use the method given on page 68 under Nickel Coins.

Another method for separating zinc and nickel, depends upon their behavior towards potassium sulphide in potassium cyanide solution.* Destroy the sulphocyanic acid by evaporation with nitric acid, add potassium hydroxide in excess to the concentrated solution of the two metals, and then add potassium cyanide until the precipitate redissolves. The zinc is now precipitated as sulphide, by adding potassium sulphide. Filter out the zinc sulphide, and boil the solution with aqua regia until the liquid no longer smells of hydrocyanic acid. This decomposes the potassium-nickel cyanide and the excess of potassium cyanide. Evaporate the free acid, and precipitate the nickel as nickelous hydroxide.

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* The salt must be pure, and a fresh solution should be used.

As the zinc sulphide may contain some potassium sulphide, it cannot be weighed directly. Dissolve the precipitate in hydrochloric acid, boil off the hydrogen sulphide, and precipitate the zinc either as carbonate or oxalate. See page 29.

ALLOY OF TIN, COPPER, LEAD, AND ZINC.

The method of analysis follows from what has been given above. First separate the tin as oxide, according to the method given under Bronze Coins, page 67, then precipitate the lead in the filtrate by evaporation with dilute sulphuric acid. After expelling the alcohol, precipitate the copper as sulphocyanate, page 23. Decompose the sulphocyanic acid in the filtrate by evaporation with nitric acid, and determine the zinc according to one of the methods given on page 29.

ALLOY OF TIN, LEAD, BISMUTH, AND CADMIUM.

WOOD'S METAL.

Separate the tin as oxide, add sulphuric acid to the filtrate to precipitate the lead as sulphate, then precipitate the bismuth as oxychloride in the filtrate from the lead sulphate.

Concentrate the filtrate from the bismuth oxychloride, and precipitate the cadmium as sulphide by passing hydrogen sulphide through the solution. Collect the precipitate on a filter that has been dried at 100° C. and weighed, wash first with hydrogen sulphide water containing a little hydrochloric acid, and then with pure water. Dry the precipitate, CdS, at 100° C. to constant weight, and calculate the metallic cadmium.

A Gooch crucible is convenient for filtering, drying, and weighing the cadmium sulphide. The precipitate must be extracted with carbon bisulphide to remove any admixed sulphur derived from the oxidation of hydrogen sulphide. A very simple extraction apparatus which may be used for a similar purpose for other sulphide precipitates, is prepared by Friedheim in the following manner. After the precipitate has been washed with alcohol to remove any water, place the crucible in a second Gooch crucible, and this on the bottom of a beaker about 15 cm. high and 12 cm. wide. Pour into the bottom of the beaker a little pure carbon bisulphide* and cover the beaker with a watch-glass filled with cold water. Set the beaker on the water-bath where it will have a temperature of about 50° C. The carbon bisulphide boils, condenses on the under side of the watch-glass, drops onto the precipitate and thus very quickly extracts the admixed sulphur. Dry the crucible at 70° C., cool and weigh. By evaporating the carbon bisulphide, the sulphur may be obtained.

Instead of determining the cadmium as sulphide, it may be separated as carbonate, and ignited to oxide, CdO. Proceed exactly as given in the determination of zinc, page 29. Befcre igniting the precipitate, it should be removed from the filter as much as possible. Moisten the filter with a solution of ammonium nitrate, dry, and incinerate it on the inverted crucible cover. Reduction of cadmium carbonate is thus avoided.

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* It should leave no residue on evaporation.

ALLOY OF TIN, LEAD, BISMUTH, AND MERCURY.

The analysis is executed as in the method given under Wood's Metal. Precipitate the mercury in the filtrate from the bismuth oxychloride, by passing hydrogen sulphide. Filter the mercuric sulphide as quickly as possible on a filter that has previously been dried at 100° C. and weighed. Wash the precipitate with water, dry at the same temperature, and weigh as mercuric sulphide, HgS.

In the separation of bismuth from mercury, by the above method, it is necessary that the mercury be present as mercuric salt. To be certain that all mercurous nitrate is oxidized to mercuric nitrate, continue the digestion with nitric acid for some time.

ALLOY OF ANTIMONY AND LEAD.

TYPE METAL.

Dissolve from 0.20–0.50 gram of the very finely divided alloy in 10–15 cc. of nitric acid, add 2–3 grams tartaric acid, and evaporate off the greater part of the nitric acid. Dissolve in water, and drop slowly into a solution which contains 20–25 grams of sodium mono-sulphide and 10 grams of sodium hydroxide, in 300 cc. of water. Warm the solution, and after the lead sulphide has settled, filter, and wash first with sodium sulphide solution, and then with hydrogen sulphide water.

Transfer the precipitate from the filter to a weighed porcelain crucible with the wash-bottle, and evaporate to dryness. Incinerate the filter in another crucible, moisten the ash with a little nitric acid, transfer to the other crucible and evaporate again almost to dryness. Cover the crucible with a watch-glass and carefully add concentrated nitric acid, drop by drop. When the violent action has ceased, evaporate to dryness and repeat the oxidation until the contents are pure white. Now add a few drops of concentrated sulphuric acid, again evaporate to dryness, ignite gently, and weigh as lead sulphate.

Add dilute sulphuric acid to the filtrate until it has a weakly acid reaction, cover the beaker and warm on the water-bath until all hydrogen sulphide is expelled.* Filter the precipitate, which is a mixture of antimony sulphide and sulphur, in an asbestos tube, and wash with hydrogen sulphide water until the filtrate leaves no residue when evaporated on platinum foil.† Dry the precipitate of antimony sulphide and sulphur at 100° C. to constant weight. Now clamp the tube in the manner described on page 47, pass through it a current of dry carbon dioxide, rotate the tube, and carefully heat until no more sulphur is evolved, and the weight of the residual antimony sulphide, Sb_2S_3, remains constant. A temperature of 260°–270° C, is sufficient to expel the sulphur; the temperature may rise to 300° C., however, without decomposing the antimony sulphide. Carbon dioxide must be passed until the tube is perfectly cold, to avoid the oxidation of the antimony sulphide. The amount of the antimony sulphide may also be determined in the mixture by decomposing with an acid, and oxidizing the hydrogen sulphide with hydrogen peroxide. The antimony is calculated from the weight of the sulphur in the barium sulphate.

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* The expulsion of hydrogen sulphide is facilitated by passing carbon dioxide or air through the solution.

† Do not neglect to test the filtrate for antimony, by passing hydrogen sulphide.

In this method, it makes no difference whether the precipitate consists of antimony trisulphide, antimony pentasulphide, or a mixture of the two, as both compounds give the same amount of hydrogen sulphide when boiled with hydrochloric acid :

$$Sb_2S_3+6HCl=3H_2S+2SbCl_3$$
$$Sb_2S_5+6HCl=3H_2S+2S+2SbCl_3$$

The same apparatus which has been described above for other purposes, may be used for this determination. The apparatus is shown in Fig. 21. The small flask in which the antimony sulphide is decomposed, is closed with a three-hole stopper. In one of the holes is inserted a suction tube, in the second a funnel tube, and in the third a tube for the introduction of carbon dioxide. The suction tube is provided with the condenser described on page 58*, and is connected with a vertical glass tube which is filled with glass beads and in which the hydrogen sulphide is oxidized by hydrogen peroxide from the dropping funnel at the upper end. The liquid which collects in the glass tube is drawn off through the glass stopcock at the lower end. Connect the apparatus with a Kipp's generator, so as to sweep all the hydrogen sulphide from the apparatus over into the tube containing the glass beads.

Place the antimony sulphide mixed with sulphur, in the flask, run in about 50 cc. of dilute hydrochloric acid through the funnel tube, and then pass a moderately strong current of carbon dioxide through the liquid. At the same time drop into the tube filled with the glass beads, hydrogen peroxide which is free from sulphuric

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* If the apparatus shown on page 58 is already set up, it may be used by passing the carbon dioxide through the funnel tube.

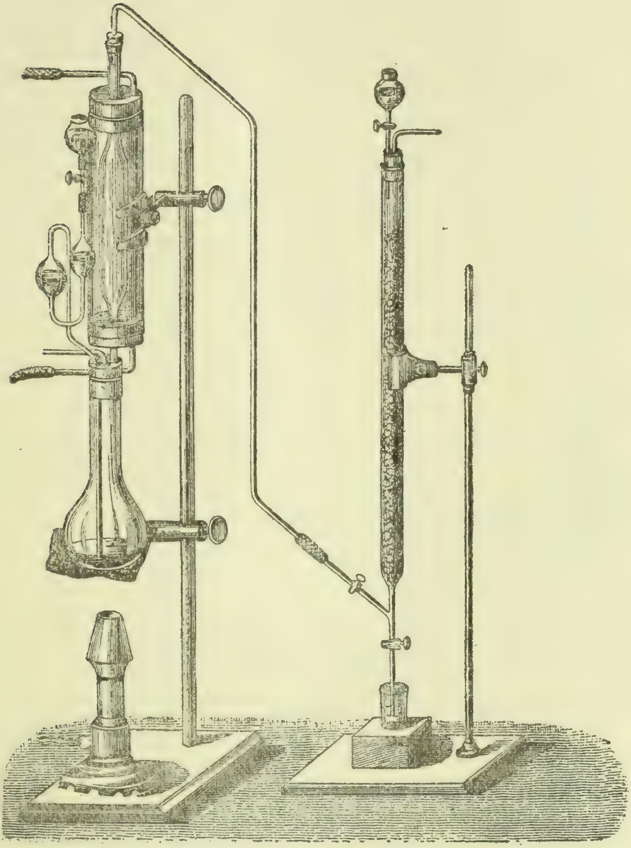

Fig. 21.

acid, and to which has been added one-third of its volume of ammonium hydroxide. When the tube is more than one-fourth full of the hydrogen peroxide, it should be drawn off through the glass stop-cock. Heat the contents of the flask to boiling, and boil for 15–20 minutes, when the sulphide should all be decomposed.

The oxidizing solution generally contains some hyposulphite besides the undecomposed hydrogen peroxide and sulphate. Boil the solution for about 5 minutes, to change the hyposulphite to sulphate, and to decompose the excess of hydrogen peroxide. Now carefully add hydrochloric acid in slight excess, and precipitate the sulphuric acid with barium chloride.

Sb_2S_3 corresponds to 3 $BaSO_4$,

therefore $BaSO_4=2/3Sb$.

Instead of the tube filled with glass beads, another absorption apparatus may be used. A very simple and useful apparatus which may be used for this purpose, and is easily prepared, is described by Arnold.* Its arrangement and use may be seen from Fig. 22.

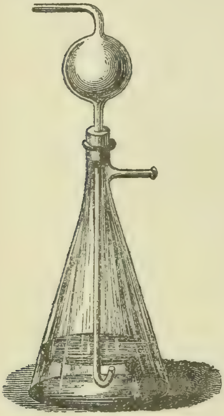

Fig. 22.

PHOSPHOR BRONZE.

Determination of Phosphorus:—Place about 2.5 grams of the bronze in a liter flask, add nitric acid (Sp. Gr. 1.40) through a funnel, and warm over a small flame until the strong action of the acid has ceased, and all of the bronze is in solution. Some varieties of phosphor bronze leave a black pulverulent residue of iron phosphide, which dissolves after warming for some time. As soon as the solution is clear, heat to boiling, and boil until the vapors are entirely colorless. It is then certain that the oxidation of phosphorous acid to phosphoric acid is complete. After cooling, add ammonium hydroxide until a clear blue solution is obtained, then pass hydrogen sulphide, until the supernatant solution appears of a decided yellow color. To separate any arsenic present, acidify the solution with acetic acid, cool, and fill the flask to the mark. Filter the solution, pipette 100 cc. into a beaker, supersaturate with ammonium hydroxide and precipitate the phosphoric acid with magnesia mixture.

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* Rep. analyt. Chem. 1885. No. 4.

The precipitate of ammonium-magnesium phosphate will be completely separated in 2 hours time, if the solution has been constantly agitated*. The further treatment of the precipitate is given on page 41.

ALLOY OF COPPER, TIN, MANGANESE, (ZINC) AND PHOSPHORUS.

PHOSPHOR-MANGANESE BRONZE.

If an alloy which contains phosphorus and tin is dissolved in nitric acid, pure stannic oxide is not formed, but a mixture of the latter with phosphoric acid. Such alloys cannot be analyzed by the usual methods. On treating the alloy with nitric acid, the substances mentioned may be in the insoluble residue. This method, however, is not to be relied upon, and it is preferable to dissolve the alloy in warm aqua regia and then precipitate the tin together with the copper, as sulphides.

Dissolve a weighed sample of the alloy in aqua regia, dilute largely with water, and precipitate the copper and tin by passing hydrogen sulphide; filter, and wash with hydrogen sulphide water.

The two metals may be separated by digesting the sulphides with yellow sodium or potassium sulphide.* Filter, wash the insoluble copper sulphide, first with a solution of the alkaline sulphide, then with hydrogen sulphide water, and determine the copper as cuprous sulphide, by ignition in a current of hydrogen. See: Determination of Zinc, page 31.

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* In laboratories where a large number of phosphorus determinations (iron ores, iron and steel, phosphates, etc.) are made daily, a shaking apparatus is used for this purpose.

Add hydrochloric acid to the filtrate from the cuprous sulphide to acid reaction, to decompose the sodium sulphostannate, and allow to stand at a gentle heat until the precipitate of stannic sulphide and sulphur has settled. As the stannic sulphide has a tendency to run through the filter it must be washed with a solution of ammonium acetate, acidified with acetic acid; continue the washing until the sodium chloride is washed out.

Dry the precipitate, and remove it as much as possible from the filter. Incinerate the latter on the inverted crucible cover, moisten with nitric acid, evaporate to dryness and ignite.

Unite the precipitate, cover the crucible, and heat for some time at a gentle heat. Now remove the crucible cover and heat more strongly, with access of air, until all the sulphur is burned off and the stannic sulphide is changed to stannic oxide. Ignite over the blast lamp, allow to cool, add a little ammonium carbonate to the crucible, and repeat the ignition to remove the last traces of sulphuric acid. Ignite to constant weight.

The tin may be determined indirectly by determining the amount of hydrogen sulphide which is liberated when the stannic sulphide is decomposed with hydrochloric acid*; for this purpose use the apparatus that was used in the indirect determination of antimony, described on page 80.

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* Dissolve a quantity of sulphur in warm potassium or sodium sulphide.

To separate the zinc from the manganese, add sodium acetate to the filtrate from the sulphide precipitate, so as to form acetates and free acetic acid, and then pass hydrogen sulphide. Treat the zinc sulphide according to the method given on page 31, and precipitate the manganese in the filtrate, with ammonium hydroxide and ammonium sulphide. See page 38. The two metals may also be separated by Hampe's method, as given under German Silver.

Determine the phosphorus in a special large sample of 2–10 grams of the alloy, as the quantity is generally quite small. Digest the sample with concentrated nitric acid until it is completely decomposed and the residue is pure white; dilute, filter out the residue of oxide and phosphate of tin, and wash it a few times. After drying, transfer it as completely as possible to a porcelain crucible, add the filter ash, and ignite; now add 3 times the amount of potassium cyanide, cover the crucible, and fuse for a few minutes at a red heat. The stannic oxide is thus reduced to metallic tin and the phosphoric acid unites with the potassium. Extract the fused mass with hot water, and the potassium phosphate together with the excess of potassium cyanide and potassium cyanate formed, pass into solution. Filter, and boil the solution with concentrated hydrochloric acid until the hydrocyanic

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* In this case it is important which sulphide of tin is present, as the amount of hydrogen sulphide obtained is not the same for equal amounts of tin:

$$Sn_2S_2 + 4HCl = Sn_2Cl_4 + 2H_2S$$
$$SnS_2 + 4HCl = SnCl_4 + 2H_2S$$

Compare equations, page 80.

acid is expelled. [This operation should be performed in a hood, as the fumes are intensely poisonous.] After cooling, pass hydrogen sulphide to precipitate the small amount of copper and tin which was redissolved by boiling the solution in the presence of excess of potassium cyanide. Add bromine water to the solution and boil, to destroy the hydrogen sulphide; now cool the solution, make ammoniacal, and precipitate the phosphorus with magnesia mixture.

As the tin and the small sulphide precipitate are easily washed, the total volume of the filtrate need not exceed 30–50 cc. so that the precipitation may be made in a concentrated solution. Agitation of the liquid accelerates the precipitation.

If the bronze contains arsenic, the greater part of it will be found in the phosphate of tin residue in the form of arsenic acid. It has been shown by experiment, however, that the arsenic acid does not go into solution as potassium arsenate, but that a part of the arsenic is reduced and volatilized, and the rest forms an alloy with the tin.

In using this excellent method, which was first mentioned by Oettel, it is only necessary that there be sufficient tin in the bronze to form phosphate with all of the phosphorus. Compare: Phosphorite. If this is not the case, and phosphorus is detected in the filtrate from the phosphate of tin on adding ammonium molybdate, a little metallic tin must be added to the sample. In most bronzes, sufficient tin will be present; there are, however, in the manufacture of bronzes, some intermediary alloys which do not contain sufficient tin to retain all of the phosphorus.

In practice, the tin in phosphor bronzes is generally determined by determining the sum of the tin and phosphorus in one sample, the phosphorus in another, and then getting the tin by difference.

ALLOY OF ANTIMONY AND TIN.

First Method, (Clarke's) :—The principle of this method is as follows : Freshly precipitated moist stannic sulphide dissolves in very concentrated boiling oxalic acid ; consequently, a boiling solution of stannic chloride which contains considerable oxalic acid, is not precipitated by hydrogen sulphide. Antimony sulphide is likewise soluble in boiling oxalic acid, but is precipitated from this solution by hydrogen sulphide.

Dissolve the alloy in aqua regia, avoiding an excess of acid, as mineral acids interfere. The excess of the acid cannot be removed by evaporation unless a sufficient amount of potassium chloride is added to form a double salt with the stannic chloride, since the latter is volatile. Now add to the solution, 20 grams of oxalic acid dissolved in 200 cc. of hot water ; dilute to 300–400 cc., heat nearly to boiling, and pass a rapid current of hydrogen sulphide for about half an hour.

The precipitate contains all of the antimony, together with a small amount of tin. Filter at once, as on long standing more stannic sulphide separates ; wash the precipitate with hydrogen sulphide water, and dissolve it in ammonium sulphide. Pour the ammonium sulphide solution into a boiling, concentrated solution of oxalic acid, and pass hydrogen sulphide while the solution continues to boil. Filter out the precipitate of antimony sulphide and sulphur, wash it as directed above, and determine the antimony as given on page 79.

Unite the filtrates in a large beaker, add ammonium hydroxide to alkaline reaction, then add ammonium sulphide and acidify with acetic acid. A stronger acid should not be used, as oxalic acid is liberated and hinders the precipitation of the stannic sulphide. Treat the stannic sulphide as given on page 84.

Second Method, (Hampe's):—Dissolve the hydrogen sulphide precipitate in the least amount of freshly prepared sodium sulphide necessary, and add sodium peroxide in small portions to the cold, concentrated solution, until the liquid is colorless, and any further addition of sodium peroxide evolves oxygen.

The solution now contains sodium stannate together with sodium hydroxide and sodium sulphate, and the antimony is precipitated as insoluble sodium antimonate. Heat the solution to boiling and then cool, add one-third the volume of alcohol, Sp. Gr. .833, and allow to stand for 24 hours for the complete separation of the sodium antimonate. Filter out the precipitate and wash it first with a mixture of equal volumes of alcohol and water and then with a mixture of three volumes of alcohol and one of water. Add a few drops of sodium carbonate solution to all the washing liquids.

To determine the antimony, dissolve the sodium antimonate off the filter with equal parts of hydrochloric acid and tartaric acid, dilute with water, and precipitate the antimony as antimony sulphide by passing hydrogen sulphide. If it is desired to weigh the antimony as the trisulphide, add a little powdered sulphur before heating in the current of carbon dioxide. See page 79.

Acidify* the alcoholic filtrate with hydrochloric acid, and precipitate the tin as stannic sulphide with hydrogen sulphide. Treat the stannic sulphide as given on page 85. Both methods are deficient in accuracy and convenience; the best method for separating tin and antimony is by electrolysis. See: Foot note, page 1.

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* If a white precipitate of sodium stannate separates, it is not nec

ALLOY OF ARSENIC AND ANTIMONY.

Bunsen's method for separating antimony and arsenic depends upon the fact that antimony only is precipitated by hydrogen sulphide from a cold solution containing arsenic and antimonic acids.

Dissolve the finely divided alloy in concentrated nitric acid, and warm to complete the oxidation; evaporate the excess of acid, and dissolve the residue in pure potassium hydroxide.* Transfer the solution to a porcelain crucible of about 150 cc. capacity, saturate with chlorine, cover the crucible with a watch-glass, and heat on the water-bath. Gradually add concentrated hydrochloric acid until in large excess, and evaporate on the water-bath to about one-half the volume. The addition of hydrochloric acid and the evaporation should be repeated until all the chlorine is expelled; finally, dilute with water and hydrochloric acid. Transfer the solution to a large beaker, dilute largely with water, and add about 100 cc. of a freshly prepared, saturated water solution of hydrogen sulphide, for each decigram of antimonic acid; all antimony will be precipitated as pentasulphide, Sb_2S_5. The excess of hydrogen sulphide must be expelled from the so-

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essary to add hydrochloric acid until it is dissolved; simply pass hydrogen sulphide, which precipitates all the tin as stannic sulphide.

* If the metals are in the form of sulphides, dissolve directly in potassium hydroxide. The potassium hydroxide should be pure (from alcohol).

lution at once, otherwise arsenic may be partially precipitated; this is best done by passing through the solution, a rapid current of air which has been filtered through cotton. About 20 minutes will suffice to remove all the hydrogen sulphide.

Filter the antimony pentasulphide with the aid of suction, on a filter which has been dried at 110° C., and weighed; wash a few times with water, then 8 times with alcohol, then 4 times with carbon bisulphide, and finally with alcohol. The filter should be filled with the washing liquid each time. Dry at 110° C., to constant weight.

Add a few drops of chlorine water to the filtrate, and heat on the water-bath; now pass a rapid current of hydrogen sulphide for some time through the hot solution, and finally allow the solution to cool, while still passing the gas. Place the solution in a warm place, and allow to stand for a day, so that the precipitate can completely separate. Filter on a dried and weighed filter, and treat exactly as given above under Determination of Antimony, to remove any traces of sulphur. Dry at 110° C., and weigh as As_2S_5.

The simplest and most accurate separation of the two metals is by electrolysis.

ALLOY OF ARSENIC, ANTIMONY AND TIN.

In the analysis of a substance which contains these three metals, it is generally preferable to separate the arsenic first, and then the other two.

The separation of arsenic from antimony and tin, depends upon its transformation into arsenous chloride and distillation as such. The method for this purpose, first used by E. Fischer, has been modified and simplified by

F. Hufschmidt, with the author's assistance*, so that it is now preferable to all former methods.

As already mentioned, the method presupposes that the arsenic is present in the solution as the volatile arsenous chloride. E. Fischer used a solution of ferrous chloride,† which, however, may be replaced by ferrous sulphate, or preferably by ferrous-ammonium sulphate.‡

Oxidize a weighed amount of the alloy with concentrated hydrochloric acid and potassium chlorate,‖ heat on the water-bath till action ceases, and evaporate to dryness. Transfer the residue with concentrated hydrochloric acid to a flask of about 500–600 cc. capacity§, add 20–25

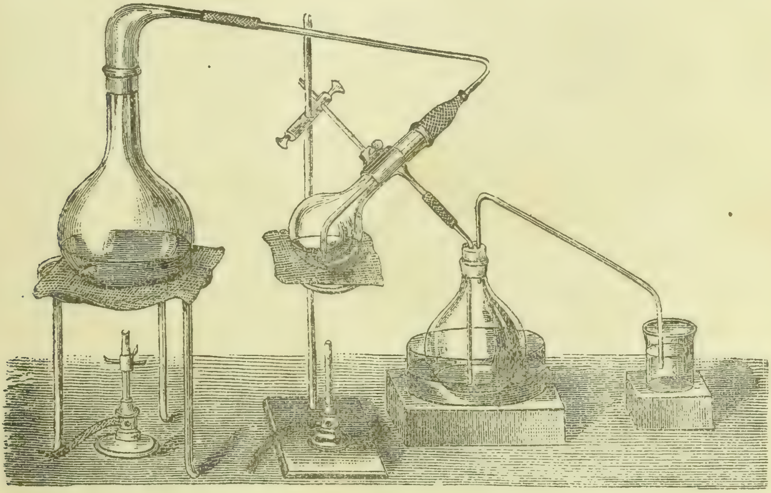

Fig. 23.

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* Ber. deutsch. chem. Gesell, Vol. 17, p. 2245.

† Pour 25 per cent hydrochloric acid on a large amount of iron filings, allow to act in the cold, and then warm. Filter out the undissolved iron and preserve the solution in glass stoppered bottles.

‡ Classen and Ludwig, Ber. deutsch. chem. Gesell, Vol. 18, p. 1110.

‖ Nitric acid cannot be used on account of its subsequent action on the ferrous salt. If it has been used, it must be removed by evaporation with sulphuric acid.

§ It makes no difference if the residue is incompletely dissolved by the hydrochloric acid.

cc. of ferrous chloride solution of about 25 grams of ferrous-ammonium sulphate, and then add concentrated hydrochloric acid until the total volume is about 200 cc. Clamp the flask at an angle of about 45° on a wire gauze, connect it on one side with a hydrochloric acid gas generator, and on the other side with an ordinary flask of about 1 liter capacity. The latter is connected with a beaker partially filled with water. The arrangement of the apparatus is seen in Fig. 23. The flask for the generation of hydrochloric acid gas, of about 4 liters capacity, contains about 500 grams of sodium chloride; to this is added an excess of sulphuric acid, Sp. Gr. 1.60.*

The flask for retaining the arsenous chloride is filled with about 400–500 cc. of water, then set in a deep vessel and cooled with water.

Hydrochloric acid gas is now generated by warming the generator, and the gas is passed into the solution until no more absorption takes place, which will require about an hour. Now heat the solution to boiling, and distill about 80–100 cc. of the solution, while passing a rapid current of hydrochloric acid gas. If the absorption flask is well cooled, not a trace of the arsenous chloride will pass over into the beaker.

The complete separation of the arsenic depends upon having the solution of the metals completely saturated with hydrochloric acid before beginning the distillation. A large quantity of arsenic (0.5 gram. As_2O_3) may be volatilized as the chloride, in one distillation.

The arsenic in the absorption flask may be determined in various ways. Either add fresh hydrogen sulphide wa-

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[* A more convenient method is to drop concentrated sulphuric acid from a dropping funnel into concentrated hydrochloric acid.]

ter and determine the arsenic as trisulphide, As_2S_3, on a weighed filter*, or oxidize the precipitate with hydrogen peroxide and determine the sulphuric acid.† In the latter case, avoid a large excess of hydrogen sulphide and remove the excess by passing carbon dioxide. When the precipitate has settled, siphon off the supernatant liquid, add ammonium hydroxide in slight excess, and then add 25 cc. of hydrogen peroxide. Heat to boiling, and continue the boiling until no more bubbles are formed; acidify with hydrochloric acid and precipitate with barium chloride. Calculate the amount of arsenic from the weight of the barium sulphate.

$$As_2S_3 = 3BaSO_4 ; \; BaSO_4 = 2/3As.$$

The arsenous acid in the distillate may also be determined volumetrically, by titration with iodine of known strength, after neutralizing with an excess of potassium or sodium carbonate.‡ See: Volumetric Analysis: Iodine and Sodium Arsenite.

To separate the antimony and tin, first remove the iron by precipitation with hydrogen sulphide; wash the precipitate, and determine the two metals in the filtrate, as given on page 87.

Piloty and Stock have modified the distillation method as follows: Instead of reducing with ferrous salt, they distill in a current of hydrogen sulphide, after saturating the solution with hydrochloric acid.

The only difference in the apparatus, Fig. 23, is that a side tube is fused into the connection between the hydrochloric acid generator and the distilling flask; the side tube is connected with the hydrogen sulphide generator by means of a rubber tube. The rubber tube should be provided with a pinch-cock near the side tube. The absorption flask contains 250 cc. of water, acidified with hydrochloric acid, and is covered with a pierced watch-glass. No loss of arsenic need be feared, as it is at once precipitated as trisulphide. The absorption flask should be cooled with ice.

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* Wash with water, alcohol, carbon bisulphide, etc., exactly as given under the determination of antimony pentasulphide. Page 90.

† Classen, Ber. deutsch. chem. Gesell, Vol. 16, p. 1061.

‡ Prepared by gently igniting the bicarbonate.

Oxidize the metals as given above, and dilute to about 100 cc. with concentrated hydrochloric acid; heat to boiling, and pass a rapid current of hydrochloric acid gas while the tube for the introduction of hydrogen sulphide is closed. As soon as all parts of the distilling apparatus have been heated to the temperature of the vapor, the pinch-cock is opened so that about 2 bubbles of hydrogen sulphide pass per second. This produces an opalescence, but no separation of sulphur, in the distilling flask.

After the solution has boiled vigorously and only a few cc. are left, the current of hydrogen sulphide is stopped. All the arsenic is now in the absorption flask, in the form of flocculent trisulphide. The latter cannot be weighed as such, because the sulphur which it contains cannot be extracted by carbon bisulphide. Dissolve in potassium hydroxide, avoiding an excess, add bromine water until a yellow color persists, acidify slightly with hydrochloric acid, incline the flask at an angle and boil until all the bromine is expelled. Cool to 70°, pass a rapid current of hydrogen sulphide for 3 hours, and continue the passage of the gas until the solution is cold.

After standing 12 hours, filter on a Gooch crucible, and extract any admixed sulphur with carbon bisulphide in the manner described on page 77. Dry the precipitate at 105° C. to constant weight, and weigh as As_2S_5.

While distillation with a ferrous salt has the advantage that the arsenic may be titrated directly in the filtrate, this method gives a residue which contains no foreign metal. This latter method is especially suited to the electrolytic separation of antimony and tin. For this purpose, it is only necessary to neutralize the solution with sodium hydroxide, evaporate to dryness and dissolve the residue in sodium sulphide solution. See the author's work cited on page 1, Foot Note.

According to Hampe, the sulphides of arsenic, antimony and tin may be dissolved in alkaline sulphide, and separated as follows : Add dilute sulphuric acid, expel the hydrogen sulphide, and filter off the mixture of sulphides and free sulphur. Transfer to a small beaker, and dissolve the precipitate adhering to the paper, with a little freshly prepared ammonium sulphide ; add the solution to the beaker containing the precipitate, decompose with hydrochloric acid and oxidize the sulphides with potassium chlorate.

After removing the free chlorine, add tartaric acid, and filter off the undissolved sulphur. On saturating with ammonium hydroxide, a clear liquid should be obtained. If this is not the case, more tartaric acid must be added. The more tin is present, the more tartaric acid is necessary.

Concentrate the solution as much as possible, and precipitate the arsenic acid with magnesia solution in the same manner as given for phosphoric acid, on page 41. After the precipitate has completely separated, dissolve it in hydrochloric acid and reprecipitate by adding ammonium hydroxide in excess.

The precipitate may either be filtered on a previously dried and weighed filter, and weighed as ammonium-magnesium arsenate, after drying at 105° C., or it may be determined as magnesium pyroarsenate.

The precipitate, when dried to constant weight at 105° C., has the composition $MgNH_4AsO_4$.

If it is desired to determine the arsenic as pyroarsenate, transfer the precipitate as completely as possible to a porcelain crucible, moisten the filter with nitric acid or a solution of ammonium nitrate, and incinerate it on the inverted crucible cover. Add the filter ash to the main body of the precipitate, moisten with nitric acid and heat at first for some time in the air-bath at 130° C. Gradually increase the temperature to 400° C. After the heating has been continued for some time, to volatilize the ammonia, the crucible is gradually heated up to a bright red heat.

As a part of the arsenic may be lost on incinerating the filter, the greater part of the precipitate of magnesium-ammonium arsenate may be transferred to a porcelain crucible and ignited as given above and weighed as magnesium pyroarsenate. The remainder of the precipitate adhering to the filter paper, may be dried at 105° C. to constant weight, and weighed as magnesium-ammonium arsenate. The total arsenic is obtained by adding the arsenic calculated from the two portions.

Good results may also be obtained as follows: Dissolve the precipitate of magnesium-ammonium arsenate off the filter with nitric acid, Sp. Gr. 1.20, evaporate the solution to dryness in a weighed porcelain crucible on the water-bath, heat carefully on the sand-bath or asbestos plate to remove ammonium salts, and finally ignite for 5 minutes at a low red heat. Weigh as magnesium pyroarsenate.

From the preceding, it follows that the determination of arsenic as pyroarsenate is complicated and tedious. It is therefore preferable to determine the arsenic as pentasulphide, as given on page 90. For this purpose, the filtrate from the sodium antimonate should first be acidified with hydrochloric acid, and the alcohol completely expelled.

Unite the filtrates from the arsenic sulphide, acidify with hydrochloric acid, and precipitate the sulphides of antimony and tin by passing hydrogen sulphide. The two sulphides may be separated as given on page 87.

Note.—If the sulphides of arsenic and tin are present in alkaline sulphide solution, they may be separated in the dry way as follows: Precipitate the sulphides as given above, and collect the precipitate on a filter which has been dried at 110° C. and weighed. Wash the precipitate with the precautions given under tin sulphide, page 84.

The arsenic and tin in the mixture of arsenic sulphide, tin sulphide and sulphur, may be determined by placing a weighed amount of the precipitate in a bulb-tube*, uniting one arm with a hydrogen sulphide generator, and bending the other arm down and immersing it in ammonium hydroxide in an absorption flask, Fig. 24. Connect the absorption flask with a U-tube, also partially filled with ammonium hydroxide, to avoid any loss of arsenic sulphide.

When the entire apparatus is filled with hydrogen sulphide, heat the bulb, at first gently and then more strongly and continue the heating as long as arsenic sulphide continues to volatilize.

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* If the weighed substance cannot be transferred to the bulb without loss, first dry the latter at 110° C., determine its weight, transfer a portion of the precipitate to the bulb, dry at the same temperature, and weigh again.

After the apparatus has cooled, cut off the bent arm of the tube close up to the bulb, and dissolve the sublimate in it with warm, dilute potassium hydroxide. Transfer the potassium hydroxide and the contents of the absorption flasks to a porcelain dish, evaporate on the water-bath, and carefully oxidize the residue with fuming nitric acid.

The contents of the absorption flask may also be supersaturated with hydrochloric acid, and the arsenic sulphide in suspension then oxidized to arsenic acid by adding potassium chlorate and warming.

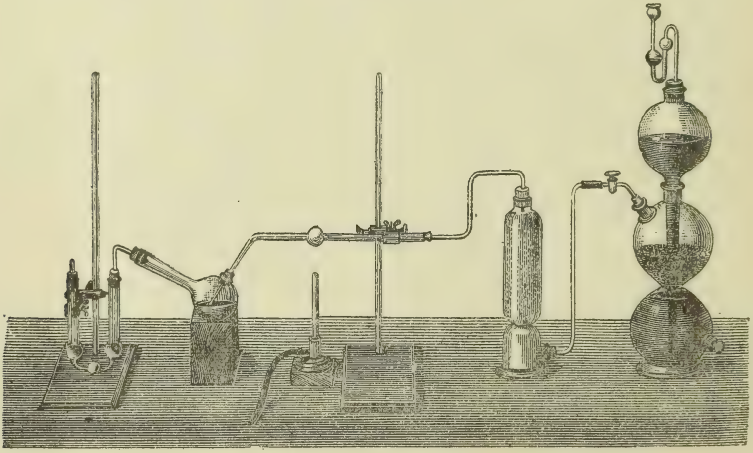

Fig. 24.

In either case, filter off the unoxidized sulphur, add ammonium hydroxide in excess to the filtrate, and precipitate the arsenic as magnesium-ammonium arsenate. Treat the precipitate exactly as given on page 96.

The tin remaining behind in the bulb as tin sulphide, may be determined as stannic oxide by transferring to a porcelain crucible, moistening with nitric acid, heating gently at first and then at a red heat. If a bulb-tube of difficulty fusible glass has been used, the sulphide of tin may be oxidized to stannic oxide by passing a current of air through the bulb, while heating at a low red heat.

SEPARATION OF BARIUM FROM STRONTIUM.

The method depends upon the following facts: Barium chromate is appreciably soluble in solutions which contain free acetic acid, or ammonium salts; if, however, enough of the precipitant, ammonium chromate, is used, so that the acetic acid will be united to the ammonium of the ammonium chromate, the barium chromate is quite insoluble.

Under these conditions almost all of the strontium chromate remains in solution. As there is always a little strontium chromate in the precipitate of barium chromate with a single precipitation, it is necessary to dissolve and reprecipitate. (Fresenius.)

The reagents required are:

1. A neutral 10.% solution of ammonium chromate.
2. A solution of ammonium acetate which contains 31 grams of the salt in 100 cc. of water.
3. Acetic acid, Sp. Gr. 1.065.
4. Nitric acid, Sp. Gr. 1.20.

Dissolve about 1 gram of a mixture of pure barium and strontium carbonates in the least amount of dilute hydrochloric acid necessary, remove the excess of acid by evaporation and dissolve in about 300 cc. of water. Now add 6 drops of acetic acid, and a few drops of ammonium acetate to neutralize any mineral acid present.

Heat the solution, and precipitate with an excess of ammonium chromate; allow to settle for an hour and decant on a small filter.

Wash the precipitate with water containing ammonium chromate, until the filtrate gives no precipitate with ammonium hydroxide and ammonium carbonate, then wash with pure warm water until the filtrate shows only a very slight reddish-brown color when tested with neutral silver nitrate.

As the precipitation must be repeated, pierce the point of the filter and rinse the precipitate into a beaker; wash the filter first with warm dilute nitric acid and then with water. Dissolve the precipitate by warming with a small amount of nitric acid, (about 2 cc.) Dilute to about 200 cc., warm, gradually add 5 cc. of ammonium acetate and then ammonium chromate until there is no odor of acetic acid. After standing for an hour, decant through a filter, digest the precipitate with hot water, and after cooling, rinse the precipitate onto the filter and wash with cold water until the filtrate gives no test for chromic acid, with silver nitrate.

Remove the barium chromate from the filter, incinerate the latter separately, and then ignite both precipitate and filter ash in a platinum crucible at a gentle heat. If the precipitate is ignited too strongly, the chromic acid will be reduced, and the residue will appear green. The particles of the precipitate which adhered to the filter paper will be reduced when the paper is incinerated but may again be oxidized to chromic acid by careful heating.

Add 1 cc. of nitric acid to the filtrate containing the strontium, concentrate, and precipitate with ammonium hydroxide and ammonium carbonate. As the precipitated strontium carbonate retains some chromic acid, dissolve it in hydrochloric acid, add to the solution an equal volume of alcohol, and precipitate the strontium with an excess of dilute sulphuric acid. After standing for 6 hours, filter, wash with dilute alcohol, ignite at a moderate temperature, and weigh as $SrSO_4$.

SEPARATION OF BARIUM FROM CALCIUM.

Separate the barium as barium chromate, by two precipitations, exactly as given in the Separation of Barium from Strontium. Add ammonium hydroxide to the filtrate to alkaline reaction, and precipitate the calcium with ammonium oxalate. Treat the calcium oxalate as given on page 21. The nitrates of the metals may also be separarated by ether-alcohol, according to the method given below.

SEPARATION OF STRONTIUM FROM CALCIUM.

This method depends upon the insolubility of strontium nitrate, and the solubility of calcium nitrate, in a mixture of equal parts of absolute alcohol and anhydrous ether.

Dissolve about 1 gram of the mixed carbonates of strontium and calcium in nitric acid in a small porcelain dish, evaporate to dryness, and heat for some time at 130° C. in the air-bath*. Finally pulverize the mass, add 5 cc. of ether-alcohol and quickly rub together. Repeat this treatment 5 times, transferring the solutions to a small flask.

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* The temperature may be raised to 180° without decomposing the salts.

After expelling the ether-alcohol from the residue, dissolve in water, evaporate to dryness, and heat for some time at 130° C. in the air-bath. Pulverize the mass, and transfer it to the flask with about 15 cc. of ether-alcohol. Allow to stand for 24 hours, with frequent shaking; filter through a small filter, and wash the strontium nitrate by decantation and on the filter, with ether-alcohol 10–12 times, using about 5 cc. of the washing solution each time. The strontium nitrate inthe flask, on the filter, and in the dish, if it was not all transferred, is now dissolved in water, and precipitated with sulphuric acid in the presence of alcohol.

Precipitate the calcium direct with sulphuric acid, in the ether-alcohol solution. Allow to stand for 6 hours, filter out the calcium sulphate, wash with absolute alcohol, heat at a low red heat, and weigh as calcium sulphate.

SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.

From what has been said in the above individual separations, two methods may be derived. First, separation of the barium as chromate, precipitating the strontium and calcium as carbonates, by ammonium hydroxide and ammonium carbonate, and then separating the strontium and calcium nitrates by ether-alcohol. Second, treating the three nitrates with ether-alcohol, which leaves barium and strontium nitrates insoluble. The barium may now be separated from the strontium by ammonium chromate.

SEPARATION OF BARIUM, STRONTIUM, CALCIUM, AND MAGNESIUM.

Magnesium may be separated from the alkaline earths by evaporating the solution to dryness, adding alcohol and then concentrated sulphuric acid in slight excess. This precipitates barium, strontium and calcium, as sulphates, while magnesium sulphate remains in solution. After the precipitate has completely settled, filter, and wash with absolute alcohol, until the filtrate gives no reaction for sulphuric acid. The precipitate should now be washed with 35–40% alcohol, to remove the small amount of magnesium sulphate that is precipitated with the alkaline earths. Expel the alcohol from the filtrate, add ammonium hydroxide in excess, and precipitate the magnesium as magnesium-ammonium phosphate.

The alkaline earths may be separated by fusing the mixed sulphates with sodium carbonate in a platinum crucible. Extract the fuse with warm water, filter, and wash the carbonates with hot water, to remove the sodium sulphate.

The barium, strontium and calcium may now be separated by one of the methods given above.

SEPARATION OF POTASSIUM FROM SODIUM.*

The separation of the two alkalies depends upon the precipitation of potassium as potassium-platinic chloride, while the sodium-platinic chloride remains in solution. To obtain exact results, definite conditions must be observed.

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* Use a mixture consisting of about 25 per cent. of sodium chloride and 75 per cent of potassium chloride.

Dissolve from .3–.5 gram of the mixed chlorides which have been dried at 100° C., in a porcelain dish, in the least amount of water necessary; add a concentrated solution of platinic chloride*, which is weakly acid with hydrochloric acid, and evaporate at a low temperature on the water-bath until the mass appears dry on cooling. Add 95% alcohol to the cold residue, stir, and decant through a filter that has been dried at 115° C. and weighed. Repeat the washing of the potassium-platinic chloride with small amounts (5 cc.) of alcohol until the filtrate appears colorless; now transfer the precipitate to the filter, and dry at 110°–115° C. to constant weight. The residue is K_2PtCl_6.

Drying a large precipitate on a filter is an operation which requires considerable time. It is much more rapid to transfer the precipitate to a weighed platinum or porcelain dish, and dry at 112° C. to constant weight. Any particles of the precipitate which adhere to the filter and cannot be removed, may be dissolved with hot water and the solution evaporated with the body of the precipitate and finally dried at 115° C., to constant weight.

Calculate the potassium-platinic chloride to KCl, subtract this weight from the weight of the mixed chlorides taken for analysis, and thus obtain the NaCl by difference.

Instead of separating the potassium as potassium-platinic chloride, the total chlorine in a weighed portion of the mixture may be determined, and the potassium chloride and sodium chloride then calculated. This indirect determination of potassium in the presence of sodium, is of general applicability and may be used whatever the proportions of the salts in the mixture.* Correct results can be obtained only when the alkaline chlorides are absolutely pure.

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* Sufficient platinum chloride must be added, not only to convert all the potassium into potassium-platinic chloride, but also all the sodium into the double salt. Otherwise the potassium-platinic chloride will be contaminated with sodium chloride which is difficult to wash out with alcohol.

If a platinic chloride solution is used which contains 10 grams platinum to 100 cc. of the solution, 10 cc. of the platinic chloride solution will suffice for .5 gram of the mixture used for analysis.

The chlorine may be estimated either by precipitating with silver nitrate and weighing the silver chloride, (See Barium Chloride p. 26), or the chlorine may be estimated volumetrically. (See Volumetric Analysis; Analysis by Precipitation.)

If S represents the sum of Potassium and Sodium Chlorides,

C the amount of chlorine found,

then,

$$x(KCl)=4.6413\ (S-1.6502\ C)$$
$$y(NaCl)=S-x.$$

MIXTURE OF POTASSIUM CHLORIDE, SODIUM CHLORIDE AND MAGNESIUM SULPHATE.

The following method, devised by the author,† for separating magnesium from the alkalies, depends upon the precipitation of the magnesium as oxalate, (page 28). In this method, it makes no difference whether the magnesium and alkalies are present as chlorides, sulphates, or nitrates. Sulphates, however, are less suitable than the two other salts.

Dissolve about .5 gram of the mixture in water, dilute to 25–30 cc., add a cold saturated solution of ammonium oxalate*, heat to boiling and precipitate the magnesium-ammonium oxalate by adding concentrated acetic acid. Allow to cool somewhat, add 1/3 the volume of alcohol to the solution, and allow to stand in a warm place for about 6 hours. Filter, and wash with a mixture of equal volumes of concentrated acetic acid, alcohol and water, and ignite to magnesium oxide.

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* In the indirect analysis of the sulphates, this is not the case, (See page 106).

† Zeit. f. anal. Chem., Vol. 18, p. 373.

The alkalies are best determined by evaporating to sulphates. Evaporate the filtrate to dryness in a platinum dish, and expel the ammonium salts by gentle ignition; moisten the residue with dilute sulphuric acid, and ignite. A mixture of neutral sulphates and acid sulphates is formed. As the acid sulphates form the neutral sulphates very slowly on ignition, add small pieces of pure ammonium carbonate during the ignition, cover and heat to constant weight. The residue consists of neutral sulphates. After the weight has been determined, dissolve in a little water, add a few drops of dilute hydrochloric acid, and precipitate the potassium as potassium-platinic chloride (page 104). Subtract the amount of potassium sulphate equivalent to the weight of the potassium-platinic chloride, from the weight of the mixed sulphates, and obtain the sodium sulphate by difference.

In some cases, the amount of sulphuric acid in the mixed sulphates may be determined, and the amount of potassium and sodium obtained indirectly by calculation.

If,

x=amount of potassium sulphate,

y=amount of sodium sulphate,

---

* If a warm saturated solution of ammonium oxalate is added to a concentrated solution of the mixed salts, the addition of acetic acid causes a precipitation of potassium-magnesium oxalate as well as magnesium oxalate. The potassium salt is difficult to wash out.

S=the weight of the mixed sulphates, and
s=the weight of sulphuric acid found (calculated as SO_3)

then,

$$
\begin{gathered}
x+y=S. \\
0.45928\,x+0.5631\,y=s \\
0.45928\,x+0.5631\,(S-x)=s \\
0.45928\,x+0.5631\,S-0.5631\,x=s \\
-0.10328\,x=s-0.5631\,S. \\
0.10382\,x=0.5631\,S-s \\
x=5.4238\,(S-1.7758\,s) \\
y=S-x.
\end{gathered}
$$

This indirect method, however, presupposes that the sodium sulphate is in considerable excess of the potassium sulphate. If the amount of potassium sulphate is in excess of, or even equal to, the amount of sodium sulphate, the result is inaccurate.*

Another method for separating magnesium from the alkalies, depends upon its precipitation as magnesium-ammonium phosphate. Dissolve the mixed salts in water, add ammonium chloride and ammonium hydroxide, and then ammonium phosphate in slight excess. Treat the precipitate as given on page 27.

Neutralize the filtrate with hydrochloric acid, and separate the phosphoric acid from the alkalies as given on page 42. Evaporate the filtrate to dryness, volatilize the ammonium salts by gentle ignition, and transform the alkalies to sulphates as given above.

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* Kretschy, Zeit. f. anal. Chem., Vol. 15, p. 56.

ALUM.

Constituents: Aluminum, Potassium, (Ammonium), Sulphuric Acid, and Water.

Determination of Aluminum and Potassium:—Place about 1.5 grams of the salt in a platinum or porcelain dish, add a little water, and warm to solution; add ammonium chloride and then ammonium hydroxide in slight excess. Heat on the water-bath until the ammonia is expelled,* filter, and wash by decantation with hot water. As the aluminum hydroxide can be washed but slowly on account of its gelatinous nature, it is convenient either to use suction, or to dry the precipitate and then continue the washing. Place the dried precipitate in a well closed crucible and ignite, at first gently and then more strongly. As aluminum hydroxide always contains aluminum sulphate† if precipitated in the presence of sulphuric acid, the precipitate must finally be heated over the blast lamp.

Evaporate the filtrate from the aluminum hydroxide to dryness in a platinum or porcelain dish, and volatilize the ammonium salts by gentle ignition, Dissolve the residue in a very small amount of water, transfer to a platinum crucible, evaporate to dryness, and ignite the residue. Add ammonium carbonate during the ignition, to facilitate the formation of normal sulphate. Weigh as potassium sulphate.

The ammonia is determined by decomposing the ammonium sulphate with potassium or sodium hydroxide and absorbing the liberated ammonia in hydrochloric acid. The apparatus shown in Fig. 25 may be used for the purpose. The tubulated retort r contains a concentrated solution of potassium or sodium hydroxide; the two absorption flasks v and v′ are partly filled with dilute hydrochloric acid. The ammonium hydroxide passes over through the condenser K.

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* [Genth and Penfield claim that washing with pure water, rather than the solubility of the precipitate in the ammonium hydroxide, causes a small amount of aluminum to pass into the filtrate. Penfield and Harper recommend washing the precipitate with a dilute solution of ammonium nitrate; 20 cc. of nitric acid, neutralized with ammonium hydroxide, to a liter. See: Am. Jour. Sci., 3d Ser., Vol. 22, p. 112, 1886.]

† For this reason the sulphuric acid cannot be determined in the filtrate from the aluminum hydroxide.

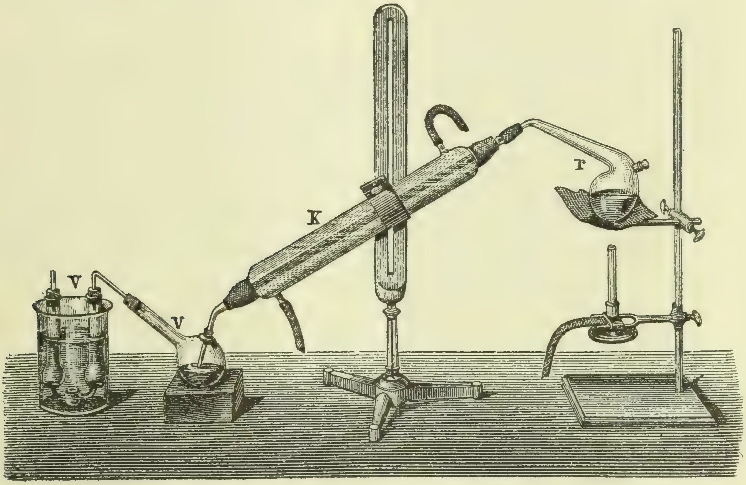

Fig. 25.

As cork or rubber may absorb ammonia, care must be taken that the latter does not come in contact with them. When the apparatus is set up, weigh a portion of the substance in a small glass tube, transfer to the retort through the side tubulure, and distil over about one-third of the contents of the retort. Determine the ammonium chloride in the absorption flask by transferring to a porcelain dish, adding platinum chloride and evaporating on the water-bath. Proceed as given in the Determination of Potassium; page 104.

If the quantity of ammonium-platinic chloride is slight, it may be ignited to metallic platinum in a weighed porcelain crucible, and the ammonium calculated from the weight of platinum.

The determination of the resulting ammonium chloride by evaporating the liquid in the absorption flasks, does not give an accurate result, as ammonia or ammonium chloride is always volatilized on evaporation and drying.

The ammonium in alum may also be determined by absorbing it in an excess of standard acid and then titrating the excess with a standard alkali solution. See Volumetric Analysis; Acidimetry.

If the alum contains iron, it may be determined in a large quantity of the salt by precipitating with potassium hydroxide, and then determining the iron in the precipitate volumetrically. See Volumetric Analysis; Potassium Permanganate and Ferrous Salts. The iron so found, calculated to Fe_2O_3, must be subtracted from the weight of Al_2O_3 found above.

The sulphuric acid is determined as barium sulphate as usual, in a special portion.

The water in alum cannot be determined by 'loss of weight on ignition,' as not only water, but sulphuric acid, and ammonia also, if present, would be volatilized. If the alum is free from ammonia, the method given under Dolomite, page 61, may be used. This method is not applicable in the presence of ammonia, as the latter would be expelled on ignition with lead carbonate, and would be absorbed by the calcium chloride. In this case, connect two U-tubes, filled with pumice stone saturated with concentrated sulphuric acid, to the tube containing the lead carbonate and alum. By the gain in weight of the previously weighed tubes, the per cent. of the water + ammonia is determined. The per cent. of ammonia determined directly, is subtracted from this quantity, to obtain the per cent. of water.

SIDERITE.*

Constituents: Ferrous Carbonate, together with Carbonates of Manganese, Calcium, and Magnesium.

In an ordinary analysis of iron ores, only iron and manganese are determined; more rarely, phosphoric acid, sulphuric acid and copper.† Calcium and magnesium are considered only when their amount is considerable.

Determination of Iron :—This determination may be made most rapidly and accurately by titration on a special sample. As pure siderite contains the iron exclusively in the ferrous condition, if the ore is dissolved without access of air, it can be titrated at once with permanganate. Dissolve from .2–.5 gram of the dried mineral in dilute sulphuric or hydrochloric acid,‡ in a flask of about 100–150 cc. capacity.

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* In the analysis of ores, furnace products, etc., it is necessary to prepare a good, average sample. The ores, etc., should be broken up to the size of peas in an iron mortar, and the sample then spread out evenly. Divide it into quadrants, and take a smaller sample with a spatula or spoon, either from opposite quadrants or equally from all four. This smaller sample can now be powdered in an iron motar, and the quartering repeated. The final sample should be ground in an agate mortar until no hard particles can be felt with the pestle.

† Spathic Iron Ore is ordinarily free from these constituents; for their determination, See: Red Hematite.

‡ Hydrochloric acid decomposes potassium permanganate, especially when heated: $KMnO_4 + 8HCl = KCl + MnCl_2 + 5Cl + 4H_2O$. The interference of hydrochloric acid will be completely avoided, if a

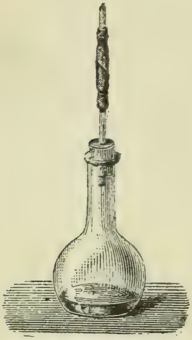

Fig. 26.

The oxidation of the iron during solution may be prevented by placing a Bunsen valve in the neck of the flask, Fig. 26; this allows vapors to escape, but does not allow air to enter. It is more convenient to use the apparatus shown in Fig. 28. After the substance and acid have been placed in the flask, add a little sodium bicarbonate and connect with a second flask or beaker which contains a solution of sodium bicarbonate. The acid is now warmed until solution is effected, and the flame then removed; on cooling, the liquid from B. is sucked back into A. As an alternative method, a current of carbon dioxide can be passed through the flask during solution, to avoid any oxidation of the iron. When the solution is complete, dilute the water (previously boiled), and titrate with permanganate. See Volumetric Analysis: Potassium Permanganate and Ferrous Salts.

If the mineral contains ferric oxide together with the ferrous oxide, the former must be reduced before titration. For this purpose, add a few pieces of zinc to the acid solution, which dissolves with an evolution of hydrogen. While the ferric iron is being reduced to ferrous, the yellow color of the former gradually disappears, and the solution finally becomes colorless. The reduction is facilitated by gentle heat. If the solution of gas becomes weak, add a little dilute sulphuric acid.

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sufficient amount of manganous chloride, or preferably, manganous sulphate, is added to the solution. Use a solution which contains 200 grams of the salt to the liter; 20 cc. of this solution will then be sufficient, even if hydrochloric acid is present in large excess. (Zimmerman).

As soon as the liquid is perfectly decolorized, and all the zinc is in solution, cool, and titrate at once with permanganate.

If a piece of platinum foil or wire is added with the zinc, reduction of the iron is effected much quicker.

Potassium permanganate can also be used to determine ferrous iron in the presence of ferric iron. Dissolve a weighed sample with exclusion of air (see above), and titrate directly with permanganate.

A second sample is reduced with zinc, and the total iron determined with permanganate. The ferric oxide is then determined by difference.

Another method for the determination of ferrous iron, which permits the use of hydrochloric acid, depends upon the oxidation of ferrous iron by chromic acid.

Chromates are decomposed by ferrous salts, the ferrous iron being oxidized to ferric, and the chromic acid being reduced to chromic salt:

$$K_2Cr_2O_7+6FeSO_4+8H_2SO_4=2KHSO_4+Cr_2(SO_4)_3$$
$$+3Fe_2(SO_4)_3+7H_2O.$$

A standard solution is prepared by dissolving 4,913 grams of dried potassium bichromate in 1 liter of water.

To standardize the solution, weigh a quantity of pure metallic iron or ammonium-ferrous sulphate, dissolve in dilute hydrochloric acid, and titrate with the standard bichromate solution to the end reaction. Potassium ferricyanide is used as an indicator. Place a few drops of the freshly prepared indicator on an oiled porcelain plate, and add a very small drop of the solution to be tested; as long as a blue precipitate or a blue coloration results, ferrous iron is present. Add bichromate until the blue color is not obtained.

Volumetric Determination of Manganese.* Volhard's Method† :—Of all the methods which have been recommended for the volumetric determination of manganese, in the presence of iron, Volhard's is the most simple and accurate.

The method is based upon the following reaction, which takes place in a hot, dilute, neutral solution containing the manganese as sulphate :

$$3MnSO_4+2KMnO_4+2H_2O=5MnO_2+K_2SO_4+2H_2SO_4.$$

If the titration is made in the absence of another metallic base, the oxidation takes place but slowly, and the end reaction is indefinite. If, however, the precipitation is made in the presence of a metallic salt (Volhard used zinc oxide), the end reaction is sharp.

From a sulphate solution, in the presence of zinc oxide, the manganese dioxide is precipitated as a reddish-brown precipitate ; in the presence of chlorides, the precipitate is voluminous and of a fuchsine-red color.

To determine manganese in solutions which contain only small amounts of iron, add to the solution of the manganese, which should not contain more than .25 gram manganese in 100 cc. of solution, 25–30 grams of zinc sulphate and acidify with a few drops of nitric acid, if the liquid is neutral. Or, first neutralize with sodium carbonate until a permanent precipitate is formed, then acidify with nitric acid and heat to boiling.‡ Now add the standard permanganate, until the pink color is permanent.

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* For the gravimetric determination of manganese, see below.

† Ann. Chem. Phar., Vol. 198, p. 318.

‡ The oxidation takes place even in neutral solution, if the materials used, especially the water, are free from organic matter. As the latter, even in small amounts, renders the neutral solution cloudy, and the end reaction difficult to see, it is preferable to acidify.

In the presence of large quantities of iron, as in iron ores, iron and steel, the iron must first be removed, as it hinders the formation of manganese dioxide, even in acid solution. For this purpose, Volhard used commercial zinc-white* which had previously been ignited in a Hessian crucible, and stirred up in water, after cooling. The zinc oxide is separated from the heavy particles and preserved in a flask filled with water.

If zinc oxide is added in excess to a solution containing ferric iron, the latter is precipitated quantitatively. To make the separation, dissolve from 3–4 grams of siderite in the least amount of hydrochloric acid necessary, oxidize the solution with hydrogen peroxide or potassium chlorate, and evaporate to dryness on the water-bath. Dissolve the residue in warm water, with the addition of dilute sulphuric acid, rinse the solution into a 500 cc. flask, neutralize the greater part of the free acid with sodium carbonate or sodium hydroxide, and then add zinc oxide stirred up in water, until all the iron is separated.† The precipitation is complete when the dark solution of basic ferric salt suddenly coagulates, and the supernatant solution appears milky. Now fill the flask to the mark with water, allow the precipitate to settle, filter through a dry, folded filter, acidify with a few drops of nitric acid, and titrate an aliquot part (100–200 cc.) with permanganate, as given above.‡

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* [Commercial zinc white frequently contains small amounts of manganese. It may be purified by adding an excess of the oxide to hydrochloric acid, precipitating out what manganese may be present by the addition of bromine, filtering, and then precipitating the zinc from the clear solution by adding ammonium hydroxide, carefully avoiding an excess. Filter, wash thoroughly and preserve for use.]

† The neutralization may also be effected with zinc oxide alone.

‡ If the precipitate is allowed to completely settle, a portion may be

According to Volhard's statements, the pink color of the end reaction, persists on standing for several days, or even on shaking and digesting on the water-bath. Meineke, however, as a result of a number of experiments, claims that the pink color soon disappears, and that on warming the solution, decoloration takes place with an evolution of oxygen; so that under some conditions, nearly 30% additional permanganate may be necessary to obtain a permanent end reaction.* He also claims that on digesting the manganese precipitate with dilute acid on the water-bath, it dissolves with an evolution of oxygen. Meineke, therefore, has modified Volhard's method as follows:

Dissolve one or more grams of the ore, according to the amount of manganese present, in hydrochloric acid, oxidize with potassium chlorate if the iron is present in the ferrous condition, and evaporate the excess of acid on the water-bath. Neutralize the solution as given under Volhard's method. In the meantime, dissolve 25–30 grams of zinc sulphate in cold water in a 500 cc. flask, and add a measured quantity of potassium permanganate more than sufficient to transform the manganese into MnO_2. To this solution, add the neutral solution containing the excess of zinc oxide and the iron precipitate in suspension, agitate, and fill the flask to the mark. After mixing, filter through asbestos. Determine the excess of potassium permanganate with a standard solution of antimonous

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drawn off with a pipette, without filtering. The error due to the volume of the precipitate, may be neglected. On titration in the presence of a precipitate, see Analysis of Pig Iron, etc.

* These observations have not been made in the author's laboratory. He can only state that the pink coloration due to the permanganate, remains for several hours, so that the end reaction can be determined with great certainty.

chloride, in an aliquot portion of the filtrate. For this purpose, add 35 cc. of hydrochloric acid to 25 cc. of antimonous chloride solution, and to this add the aliquot portion of the filtrate containing the potassium permanganate. As more antimonous chloride was used than was necessary for the reduction of the permanganate, the solution still contains undecomposed antimonous chloride. This may be titrated back with standard potassium permanganate solution.

This method requires standard solutions of potassium permanganate and antimonous chloride.

Preparation of the Permanganate Solution. (Volhard):

If exactly 3.833 grams of pure, dry potassium permanganate are dissolved in one liter of water, 1 cc. of the solution corresponds to 2 milligrams of manganese. As distilled water usually contains substances which reduces the permanganate, a greater quantity of the salt, about 3.85 grams should be dissolved in a liter, and after standing for about 8 days, it may be standardized. This solution may be used for other purposes, for example, the determination of iron.

If the strength of the solution is known in terms of metallic iron, its strength in terms of manganese may be obtained by multiplying the former by .2942*

Volhard prefers to standardize the permanganate solution iodometrically, and uses a solution of sodium thicsulphate containing 30.061 grams of pure crystallized sodium thicsulphote in a liter. 1 cc. of this solution is

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* $$10\,FeO + Mn_2O_7 = 5Fe_2O_3 + 2MnO$$

From this equation, and from what is given on page 114, it follows that, 10 Fe (or 558.8): 3Mn (or 164.4) = 1: X,

from which, X = 0.2942.

equivalent to 2 milligrams of manganese. See Volumetric Analysis; Iodine and Sodium Thiosulphate.

For the iodine solution, dissolve 1.5394 grams of dry, crystallized iodine in potassium iodide, and dilute to 1 liter. 10 cc. of this solution are reduced by 1 cc. of the sodium thiosulphate solution.

The potassium permanganate may be standardized as follows: Place about 10 cc. of potassium iodide solution (5–6 grams of the crystallized salt in water) in a beaker, dilute with 150–200 cc. of water, and add about 5 cc. of pure hydrochloric acid. Stir, and add drop by drop, a measured amount (about 20 cc.) of the potassium permanganate solution. Now reduce the liberated iodine by adding an excess of sodium thiosulphate, and determine the excess of the latter by standard iodine solution.

The factor of the permanganate is obtained by subtracting one-tenth of the number of cubic centimeters of iodine solution used, from the amount of thiosulphate added, and dividing this quantity by the number of cubic centimeters of permanganate used.

Potassium permanganate may also be standardized with equal accuracy and much more simply, by using metallic iron, or pure oxalic acid.* If oxalic acid is used, one part by weight of the crystallized acid corresponds to 0.26157 parts by weight of manganese.†

Preparation of the Antimonous Chloride Solution, (Meineke):—An antimonous chloride solution of any arbitrary strength may be used, as it is only necessary to know the relation existing between it and the permanganate solution. A suitable solution may be obtained by dissolving about 15 grams of antimony trioxide in 300 cc. of hydrochloric acid, Sp. Gr. 1.19, and diluting to 1 liter.

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* See Volumetric Analysis: Potassium Permanganate and Ferrous Salts.

† $5\,[H_2C_2O_4 \,.\, 2H_2O] + Mn_2O_7 = 2MnO + 10\,CO_2 + 15\,H_2O$.

From this equation, and from what is given on page 114, the following is obtained: $5\,[H_2C_2O_4 \,.\, 2H_2O]$ (or 628.5): 3Mn (or 164.4) = 1 : X, from which X = 0.26157.

Determine the relation between the potassium permanganate and antimonous chloride solutions by adding 35 cc. of hydrochloric acid to 25 cc. of the antimonous chloride solution. Titrate with potassium permanganate to the end reaction. It is to be noted that the pink color of the permanganic acid soon disappears.

Gravimetric Determination of Manganese, Calcium, and Magnesium :—The determination of these elements requires the previous separation of the iron, which must be present in solution in the ferric condition, Any one of the following three methods may be used for separating the iron.

Separation of the Iron as Basic Carbonate :—Dissolve a weighed amount (1.5–2.0 grams) of the dried ore in hydrochloric acid, with the addition of a little nitric acid or hydrogen peroxide. Cool the solution, dilute*, add an excess of ammonium chloride, neutralize the greater part of the free acid with ammonium hydroxide and then add a dilute solution of ammonium carbonate. The precipitate produced by the latter reagent at first, dissolves on stirring the solution. Add more ammonium carbonate, drop by drop, until there is a very slight permanent precipitate on standing. If too much of the ammonium carbonate has been added, dissolve with a few drops of acetic acid, using no more of the latter than is necessary to dissolve the precipitate. Now boil the solution as long as carbon dioxide is evolved. The basic ferric carbonate precipitated settles quickly and may be washed with hot water by decantation. Add a few drops of ammonium hydroxide to the wash water.

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* The separation from manganese is complete only when there is not more than 3 to 4 grams of ferric iron in a liter of the solution.

If the solution was not exactly neutral, or if too much acetic acid was used to dissolve the precipitate, part of the iron may remain in solution. This may be detected by the yellow color of the supernatant liquid.

In this case, add ammonium hydroxide drop by drop, to weak alkaline reaction* and allow the precipitate to settle.

Separation of the Iron as Basic Acetate :—Dilute the solution containing the iron in the ferric condition, exactly neutralize with sodium carbonate as given above, add about 2–3 grams of sodium acetate, and heat to boiling†. Proceed as given above.

Separation of the Iron as Basic Sulphate.‡ Neutralize the solution containing the ferric iron with sodium carbonate, and then add 1–1.5 times as much crystallized sodium sulphate as there is iron present. The precipitate

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[*] An excess of ammonium hydroxide should be avoided, otherwise manganese hydroxide may be precipitated on standing.

[†] A neutral solution of ferric iron reacts with sodium acetate to form ferric acetate, which on boiling decomposes into insoluble basic ferric acetate and free acetic acid. This is not the case with manganous salts. The reaction is as follows:

$$Fe_2Cl_6 + 6\ Na\,(C_2H_3O_2) = 6NaCl + Fe_2\,(C_2H_3O_2)_6\ ,$$

Then,

$$Fe_2\,(C_2H_3O_2)_6 + 4H_2O = Fe_2\,(OH)_4\,(C_2H_3O_2)_2 + 4C_2H_4O_2\ .$$

Similarly, under definite conditions, neutral solutions containing a carbonate are decomposed by boiling, into basic carbonate, or in the presence of a sulphate, into a basic sulphate. If phosphoric acid is present in the solution, it is precipitated with the iron. In this case the precipate is a mixture of basic acetate and phosphate.

[‡] Kessler, Zeit. f. anal. Chem., Vol. 18, p. 1. *et seq.*

settles out completely if left to stand for some time in a cool place. Filter, and wash with warm water. Add a few drops of hydrochloric acid to the filtrate, concentrate to about 250 cc., and separate the manganese as manganous sulphide.

The precipitation must be made in a closed flask to prevent the calcium from being precipitated by the carbon dioxide of the air. After precipitation, fill the flask with boiled water, stopper and allow to stand for 12 hours. As ammonium sulphide which has stood for some time contains a large amount of ammonium thiosulphate, which causes a precipitation of calcium thiosulphate, a freshly prepared solution should be used.

Acidify the filtrate from the manganous sulphide with hydrochloric acid, warm until the liquid is clear, and then filter out the sulphur. Make the solution alkaline with ammonium hydroxide, and precipitate the calcium as calcium oxalate. Precipitate the magnesium as ammonium-magnesium phosphate in the filtrate from the calcium.

If the iron has been separated from manganese with sodium acetate, the manganese may also be precipitated with hydrogen peroxide. Add 5–10 cc. of hydrogen peroxide to the hot filtrate, supersaturate with ammonium hydroxide, and stir. Filter, wash the precipitate, and ignite to Mn_3O_4, or, add a few drops of sulphuric acid and ignite to $MnSO_4$.

The manganese may also be oxidized by bromine instead of hydrogen peroxide. It is most expedient to pass air saturated with bromine vapor through the solution containing free acetic acid. Treat the precipitate as given above. The carbon dioxide may be determined as given on page 56.

RED HEMATITE.

The Mineral, if pure, consists of Ferric Oxide, Water and Insoluble Matter. It generally contains, however, appreciable amounts of Manganous Oxide, Copper Oxide, Alumina, Calcium and Magnesium Oxides, and Phosphoric and Titanic Acids.

If the mineral contains only the first mentioned constituents, the ferric oxide may be determined as follows: Finely pulverize and dry the substance at 100° C., dissolve about .2–.3 gram in strong hydrochloric acid and determine the ferric oxide exactly as given under Siderite, page 111.*

Another method of determining the iron volumetrically, which requires the iron to be present in the ferric condition, is based upon the reduction of ferric chloride to ferrous chloride by a standard solution of stannous chloride. See Volumetric Analysis: Potassium Permanganate and Ferrous Salts.

The mineral should be dissolved in a large flask to avoid volatilization of ferric chloride.

According to Hempel, iron ores are not always completely decomposed by digestion with hydrochloric acid; the residue must therefore be fused with sodium carbonate, the fused mass dissolved in dilute hydrochloric acid, and this solution added to the main solution. Hempel avoids this operation by mixing about .3 gram of the finely pulverized ore with .4 gram of sodium carbonate and .2 gram of precipitated calcium carbonate, and fusing, after mixing in an agate mortar. Any ferrous iron present is oxidized to ferric, and the total iron may be titrated with stannous chloride. Ignite the mixture in a platinum crucible for about half an hour, with access of air. After cooling, dissolve the fuse in concentrated hydrochloric acid and titrate.

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* If titanic acid is present in the solution, the reduction of the iron with zinc also reduces the titanic acid, giving the solution a bluish-violet color. In such a case, the iron can be determined with permanganate or stannous chloride only after previous separation of the titanic acid. Otherwise the results for iron will be too high See Determination of Titanic Acid.

When the ore is fused with sodium carbonate, manganese, if present, forms sodium manganate. The latter can sometimes be detected by the green color of the fused mass. When manganese is present, the hydrochloric acid solution must be boiled in a large flask until all chlorine is expelled. Manganese is then present as manganous chloride.

Determination of Insoluble Matter, Alumina, Manganese and Copper :—Dissolve a sample of the mineral in hydrochloric acid, remove the excess of acid by evaporation, dilute with water and filter out the insoluble matter. Precipitate the copper as cuprous sulphide, by passing hydrogen sulphide through the filtrate. Treat the copper sulphide as given on page 64.

Remove the hydrogen sulphide by boiling the solution, oxidize with hydrogen peroxide or nitric acid, and separate the iron from the manganese, etc., according to one of the methods given under Siderite.

The iron precipitate contains all the alumina and phosphoric acid. To determine the alumina in the precipitate, proceed as follows : Dissolve the precipitate in hot hydrochloric acid, and pour the solution into a boiling solution of 1 part sodium hydroxide (prepared from sodium) and 2 parts water, in a platinum dish.

On boiling, the aluminum hydroxide dissolves, while the ferric hydroxide and ferric phosphate remain undissolved. The alumina may be precipitated in the filtrate by ammonium hydroxide, after acidifying with hydrochloric acid.

The manganese, calcium, and magnesium, may now be determined in the filtrate, as given under Siderite.

For the determination of phosphoric acid, dissolve about 5 grams of the ore in hydrochloric acid, filter off the insoluble matter, and evaporate to dryness.

Moisten the residue with nitric acid, and precipitate with ammonium hydroxide. Dissolve the precipitate in warm nitric acid, and separate the phosphoric acid with ammonium molybdate.

Sulphuric acid may be determined by fusing a weighed sample of the ore with an equal weight of potassium-sodium carbonate. Extract the fused mass with water, filter, and wash the residue with water containing a little sodium carbonate. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and heat for some time on the water-bath. Add dilute hydrochloric acid, warm, dilute with water, and filter out the silica. Precipitate the sulphuric acid in the filtrate, with barium chloride. The sulphuric acid may also be determined directly in the hydrochloric or nitric acid solution of the ore, according to the method given under Ferrous Sulphate, page 24.

To determine the titanic acid*, dissolve a weighed sample of the ore in hydrochloric acid, evaporate to dryness and separate the silica. Digest the residue with dilute hydrochloric acid, filter out the silica and insoluble matter, and wash it with dilute hydrochloric acid. The filtrate contains all the titanic acid. Add ammonium hydroxide in slight excess, filter out the precipitate consisting of ferric hydroxide, titanic acid, etc., and wash it with hot water. Dry and pulverize the precipitate, mix it with several times its weight of potassium bisulphate and fuse for some time in a platinum crucible. Allow the fused mass to cool, dissolve it in cold water, and reduce the iron either by hydrogen sulphide or sulphur dioxide. When the liquid is colorless, heat to boiling and pass carbon dioxide through the boiling solution, replacing the water as it evaporates. This precipitates the titanic acid. Filter out the precipitate, wash it with water, and ignite, after adding a little solid ammonium carbonate. Weigh as TiO_2.

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* [Compare the method given under Magnetite.]

The iron and titanium may also be separated by a method proposed by the author.* The separation depends on the behavior of titanic acid toward hydrogen peroxide in the presence of an excess of potassium hydroxide. Dissolve the ore in hydrochloric acid, and precipitate as usual with ammonium hydroxide. Dissolve the precipitate of ferric hydroxide and titanic acid in hydrochloric acid, add about 50 cc. of hydrogen peroxide, 25 cc. of potassium hydroxide, Sp. Gr. 1.50, dilute to 500–1000 cc., according to the amount of the precipitate and then allow the ferric hydroxide to settle. The titanium remains in solution. As the iron precipitate clogs the pores of the filter and hinders the filtration, it is desirable to dilute the solution to a definite volume. Pour into a beaker, allow to settle, and then siphon off and filter an aliquot part; if only a small amount of ferric hydroxide is precipitated, the solution may be filtered directly. Wash the precipitate with a mixture of hydrogen peroxide and potassium hydroxide in water (about 10%), and continue the washing until a few cc. of the filtrate does not appear yellow when acidified with hydrochloric acid. Heat the alkaline filtrate containing the titanium, in a covered dish on the water-bath, to destroy the excess of hydrogen peroxide. Any yellow precipitate which settles out at this point, consists of titanium trioxide mixed with titanic acid. When the evolution of gas has ceased, acidify with hydrochloric or nitric acid, heat until the yellowish-red solution is entirely colorless, and add ammonium hydroxide in very slight excess.

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* Ber. deutsch, Chem. Gesell, 1888, p. 370.

Filter out the precipitated titanic acid, wash it with hot water, ignite, and weigh as TiO_2.

The iron may be determined in the precipitate produced by potassium hydroxide, by dissolving in the least amount of sulphuric acid necessary, transforming it into iron-ammonium oxalate and then electrolizing the solution.* Pure metallic iron is obtained. If the ferric hydroxide was not perfectly free from titanic acid or alumina, they will be in suspension in the solution, as titanic acid or aluminium hydroxide. If the iron solution or the hydrogen peroxide contains silica, the latter passes more or less into the titanium procipitate. This may be removed by moistening the ignited precipitate with dilute sulphuric acid, adding hydrochloric acid, and evaporating to dryness. Re-ignite, and weigh as TiO_2.

In determining moisture in Hematites which contain carbonates, it should be noted that the water cannot be determined by 'loss on ignition,' but must be determined by direct weighing. See page 61.

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* See: Foot Note, p. 1.

LIMONITE.

Constitutents : Hydrated Ferric Oxide, together with Manganous Oxide, Alumina, Calcium and Magnesium Oxides, Phosphoric Acid, Silica, Sulphuric Acid, Titanic Acid and Insoluble Matter.

The analysis may be made exactly as given under Siderite, or Hematite.

If it is desired to make special determinations of silica and insoluble matter, proceed as follows : Boil the insoluble residue obtained as given above, for some time in a platinium dish with sodium carbonate to which has been added a little pure potassium hydroxide. Filter off the undissolved residue on a dried and weighed filter. Wash, first with hot water, then with dilute hydrochloric acid and finally with pure water. Dry the residue at 100° C., to constant weight. Acidify the filtrate containing the silica, with hydrochloric acid, and evaporate to dryness. Moisten the perfectly dry residue with hydrochloric acid, dilute with water, and filter out the silica. After washing with hot water, ignite strongly in a platinum crucible, and weigh as SiO_2.

The water may be determined by ignition, or, if carbonates are present, according to the method given on page 62.

CLAY IRON ORE.

Ferric Oxide, Alumina and Water.

If the mineral is completely decomposable by hydrochloric acid, i. e., if the argillaceous residue is free from iron after digestion with acid, the iron can best be determined volumetrically. See Volumetric Analysis, Oxidation and Reduction.

Filter out the insoluble residue, wash it with water, ignite and weigh.

If the material is not decomposable by acid, it must be decomposed by fusion. Mix the finely pulverized substance with 4–5 times its weight of sodium carbonate, or a mixture of 5 parts of sodium carbonate and 7 parts of potassium carbonate, and heat until in quiet fusion. After cooling, dissolve the fused mass in hydrochloric acid and determine the iron volumetrically with stannous chloride.

Alumina, calcium and magnesium oxides may be determined as given under Siderite.

Determine the water by igniting a sample of the dry material.

MAGNETITE.

Ferric and Ferrous Oxides, (Titanic Acid).

The analysis may be executed in various ways.

First Method :—Dissolve a weighed sample of the very finely pulverized mineral in hydrochloric acid, in an atmosphere of carbon dioxide, and determine the ferric iron with stannous chloride. Dissolve a second portion of the substance in hydrochloric acid, with the addition of a little potassium chlorate, and determine the total iron by precipitating with ammonium hydroxide and igniting to ferric oxide.

Second Method :—Dissolve a sample in an atmosphere of carbon dioxide, determine the ferrous iron with permanganate, and then the total iron, in the same solution, with stannous chloride. Or, after determining the ferrous iron with permanganate, the total iron may be reduced with zinc and then titrated with permanganate.

The ferric iron may then be calculated from the second addition of permanganate.

Or, determine the ferrous iron with permanganate in a weighed sample, and the ferric iron with stannous chloride in a second weighed sample.

See pages 122, and 124, for the determination of titanic acid and its influence on the volumetric determination of iron. See the analysis of Siderite and Hematite, for the determination of other constituents that may be contained in the Magnetite.

[Gooch's Gravimetric Method for Titanium:—After removing the silica, the next step is to remove the iron. This is best done by adding tartaric acid, reducing the iron with hydrogen sulphide, then adding ammonium hydroxide until alkaline and precipitating the iron with ammonium sulphide. If the iron is not thus reduced before precipitation, titanium will be in part thrown down also. The amount of tartaric acid necessary, depends upon the amount of oxides to be held in solution, and 3 times this weight is ample. Filter out the ferrous sulphide, and destroy the tartaric acid as follows:

Potassium permanganate to the extent of two and one-half times the weight of the tartaric used is made into a strong solution, and to the ammoniacal filtrate from the iron sulphide enough sulphuric acid is introduced to leave some excess after all the permanganate has been reduced. After expulsion of the hydrogen sulphide by boiling, the permanganate is added gradually to the hot solution contained in a large beaker or flask. A vigorous reaction ensues. When a permanent brown precipitate of manganic hydroxide appears, the tartaric acid has been fully decomposed; dissolve the precipitate with a few drops of ammonium bisulphite or of sulphurous acid solution.

Ammonium hydroxide is then added in slight excess, followed at once by acetic acid in considerable excess, and the boiling is continued for a few minutes. Thereby the titanium is freed from most of the alumina, and from calcium and magnesium if they had not been earlier removed, also from most of the manganese introduced. Filter, and wash with water containing acetic and sulphurous acids, then ignite, fuse with sodium carbonate and leach with water, to remove phosphoric acid and most of the remaining alumina. The residue is again ignited and fused with sodium carbonate. Allow the fused mass to cool, add sulphuric acid to the crucible and warm until the fuse dissolves. Pour the solution into a small volume of cold water, heat nearly to boiling and precipitate the small amount of platinum with hydrogen sulphide.

After filtering and cooling, add ammonium hydroxide until the titanium is just precipitated, and then add a measured volume, containing a known weight, of sulphuric acid—just enough to redissolve the precipitate. The solution is then made up with acetic acid in such amount that the final bulk shall contain from 7 to 11% of absolute acid, and then enough solid sodium acetate is stirred in to more than take up the sulphuric acid introduced. Upon rapidly bringing the solution to boiling, the titanium is precipitated in a flocculent and easily filterable condition, and the precipitation is complete after a minute's boiling, provided all the prescribed conditions have been followed, and zirconium is absent.

Filter, wash the precipitate with 7% acetic acid, and then with hot water. After 15–20 minutes ignition over a good burner, cool and weigh. For large amounts of titanium, the sodium carbonate fusion should be repeated. Compare: Hillebrand, Bull. U. S. Geol. Surv., No. 176, p. 71.]

BOG IRON ORE.

The constituents are: Hydrated Ferric Oxide, Ferric and Ferrous Silicates, Manganous Oxide, Alumina, (Copper Oxide), Calcium and Magnesium Oxides, Sulphuric Acid, Phosphoric Acid, Arsenic Acid, Organic Matter and Sand.

The method of analysis follows from the preceding analysis of Siderite and Hematite. It is convenient to use a separate sample for the determination of arsenic acid. Use Fischer's modified method as given on page 91. The residue in the distilling flask may be used for the determination of copper. Dilute with water, saturate with hydrogen sulphide, and ignite the precipitated cuprous sulphide in a current of hydrogen.

The moisture cannot be determined accurately, either by ignition or absorption, as the hydrogen from the organic matter is oxidized to water by the lead dioxide.

The moisture and the organic matter may be determined together by drying a sample over sulphuric acid and then igniting in a platinum crucible.

PYROLUSITE.

The naturally occurring Ore is a mixture of Manganese Dioxide, Hydrated Manganese Oxide, Ferric or Ferrous Oxide, Quartz, Clay, Calcite, etc.

The commercial value of the ore depends solely upon the presence of those oxides which will liberate chlorine.

The moisture may be determined by drying a weighed sample of the ore at 120° C., to constant weight. The drying may be considerably hastened by heating the sample in a metallic dish and stirring with a thermometer until the temperature reaches 110° C. (Mohr). As the dried ore quickly re-absorbs moisture from the air, the sample should be placed in a bottle with a ground glass stopper before cooling. Use the dried mineral for the analysis.

Various methods have been proposed for the determination of manganese dioxide in Pyrolusite. Only those methods that have come into general use will be given here.

Bunsen's Method :—If manganese dioxide is warmed with hydrochloric acid, manganous chloride and chlorine are formed :

$$MnO_2 + 4\ HCl = MnCl_2 + 2\ Cl + 2\ H_2O.$$

By passing the liberated chlorine into a solution of potassium iodide, an equivalent amount of iodine is liberated and the latter may then be determined with sodium thiosulphate. See Volumetric Analysis ; Sodium Thiosulphate and Iodine Solution.

Proceed exactly according to the method given under the above section of Volumetric Analysis, and use the apparatus shown there, for the decomposition of the pyrolusite. In the calculation, it should be remembered that, $2\ I = 2\ Cl = MnO_2$.

Fresenius' and Will's Method :—Manganese dioxide in the presence of oxalic acid and excess of sulphuric acid, decomposes as follows :

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2\ CO_2 + 2H_2O.$$

One molecule of manganese dioxide thus corresponds to two molecules of carbon dioxide.

Use 2–4 grams of the ore for the determination, according to its richness, and use the apparatus shown in Fig 27.

A, is a small flask of about 150 cc. capacity, b, a tube filled with glass beads and c, a U-tube filled with calcium chloride. The glass tube d, should reach almost to the bottom of the flask, and is closed on the upper end with a piece of rubber tubing and a short piece of glass rod.

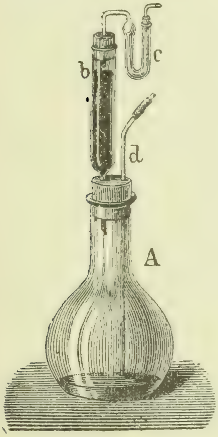

Fig. 27.

After placing the weighed sample of pyrolusite in the flask A, add about 50 cc. of water, 4–5 cc. of concentrated sulphuric acid and then quickly insert the stopper with the absorption tubes. If the pyrolusite contains carbonates, these will be decomposed by the sulphuric acid. In this case, remove the tube d from the liquid, and replace the carbon dioxide in the flask with air, by suction on the tube d. When the carbon dioxide is all removed, weigh. (Mohr).

4–5 grams of crystallized oxalic acid will be sufficient for the decomposition of 3 grams of pyrolusite.

After the apparatus has been weighed, quickly add the necessary amount of oxalic acid to the flask and stopper at once. The carbon dioxide evolved is completely dried by the sulphuric acid adhering to the glass beads, as well as by the calcium chloride in the tube c. When the evolution of gas has almost ceased, warm the flask until the action is complete.

Cool the apparatus, remove the cap from tube d, replace the carbon dioxide in the flask with air by suction on the tube c, and weigh the apparatus again.

Third Method :—The following method, known as the 'Iron Test,' is used quite extensively in England for the valuation of manganese ores.

The method depends upon the following facts: When manganese dioxide is warmed with hydrochloric acid, manganous chloride and chlorine are formed. If the liberated chlorine is allowed to act on a ferrous salt, a corresponding amount of ferric salt is formed. One molecule of MnO_2 changes 2 molecules of a ferrous salt to ferric salt:

$$MnO_2 + 4HCl = MnCl_2 + 2Cl + 2H_2O;$$
$$2FeCl_2 + 2Cl = Fe_2Cl_6.$$

If a definite amount of iron in the form of ferrous-ammonium sulphate, $FeSO_4.(NH)_2SO_4 + 6H_2O$, is used, it is only necessary to titrate the unoxidized ferrous salt with potassium permanganate, to determine the amount

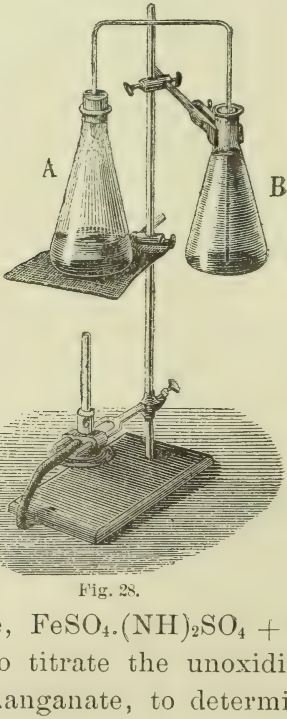

Fig. 28.

of manganese dioxide in the ore. See Volumetric Analysis.

Use the apparatus shown in Fig. 28.

A and B are 2 small flasks connected with a glass tube bent twice at right angles. The flask B is partly filled with water, or preferably with a solution of sodium carbonate, and the glass tube should reach almost to the bottom. Place the weighed amount of ferrous-ammonium sulphate in the flask A, add hydrochloric acid, connect the two flasks and warm. When the salt is in solution, remove the stopper from the flask A, and quickly add 0.5–0.6 gram of the pyrolusite in a small tube, and stopper the flask at once. Warm until a clear, yellow solution is obtained. Remove the flame, and the water or the sodium carbonate solution soon sucks back from B into A, and cools the contents of the flask. The unoxidized ferrous iron may now be titrated with potassium permanganate.

PSILOMELANE.

Constituents: Manganous Oxide, Copper Oxide, Ferric Oxide, Alumina, Nickelous Oxide, Cobaltous Oxide, Barium and Calcium (Magnesium) Oxides, Potassium, Sodium and Lithium Oxides, and Water.

For a complete analysis, dissolve a weighed amount of the mineral in hydrochloric acid, and remove the excess of acid by evaporation. Precipitate the barium as sulphate with dilute sulphuric acid, and then precipitate the copper in the filtrate by passing hydrogen sulphide.

Boil the filtrate from the cuprous sulphide to expel the hydrogen sulphide, and then oxidize the ferrous iron with hydrogen peroxide or nitric acid. Precipitate the iron and aluminum as basic carbonates or acetates, as given on page 119. The precipitate should be dissolved in hydrochloric acid and reprecipitated with ammonium hydroxide. The iron and aluminum may be separated with sodium hydroxide as given on page 123.

Concentrate the filtrate if necessary, and add yellow ammonium sulphide in slight excess. When the sulphides of manganese, cobalt and nickel have settled, filter, and wash with water containing hydrogen sulphide; the precipitate should not be exposed to the air more than necessary. Set the filtrate aside, pierce the point of the filter and wash the precipitate as much as possible into a porcelain dish. Separate the sulphides of manganese, cobalt and nickel, by treating them with a 1 part hydrochloric acid, Sp. Gr. 1.12, and 6 parts hydrogen sulphide water. Warm on the water-bath, filter quickly, and wash the residue with hydrogen sulphide water to which has been added a few drops of hydrochloric acid. All of the manganese is in the filtrate and may be precipitated and determined as given on page 38*.

Roast the sulphides of cobalt and nickel, which were insoluble in hydrochloric acid, with access of air, and then reduce the oxides in a current of hydrogen. The amount of nickel is generally too slight to determine separately; if it is desired to make the separation, however, the potassium nitrite method may be used.

Jannasch separates manganese from nickel and cobalt as follows: Dissolve the sulphides of the 3 metals in hydrochloric acid, expel the excess of acid by evaporation, and gradually add to a cold solution consisting of 9 parts of water, 2 parts of sodium hydroxide and 1 part of potassium cyanide. A platinum dish should be used, and the liquid constantly stirred while adding the chloride solution. The precipitate first formed redissolves, and at most only a slight precipitate of manganese dioxide remains undissolved. Add an excess of 3–5% hydrogen peroxide to the solution of the double cyanides, cover the dish and digest for half an hour on the water-bath. Dilute the liquid considerably, allow the precipitate to settle, filter, and wash with boiling water. Dissolve the hydrated manganese dioxide off the filter with a warm mixture of hydrochloric acid and hydrogen peroxide, precipitate the manganese again with ammoniacal hydrogen peroxide, and finally ignite and weigh the precipitate as Mn_3O_4.

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* For the volumetric determination of manganese in the presence of other metals, see Siderite, page 114.

A double precipitation is required on account of the contamination of sodium salts. The weighed precipitate should be tested for iron (from the potassium cyanide), and silica, after dissolving in dilute nitric acid and hydrogen peroxide.

Acidify strongly with sulphuric acid, evaporate to dryness and expel the excess of acid by heating; this decomposes the cobalt-potassium cyanide. The residue may now be dissolved in water, and the cobalt and nickel determined together, or separately, as usual.

To determine the calcium and magnesium, use the original filtrate from the sulphides of cobalt, nickel and manganese. Acidify with hydrochloric acid and heat to expel the hydrogen sulphide. Filter off the liberated sulphur, and precipitate the calcium as oxalate, and the magnesium as ammonium-magnesium phosphate.

It is necessary to expel the ammonium salts before precipitating the magnesium, if accurate results are to be obtained. Evaporate the solution to dryness and heat until all ammonium salts are volatilized. Dissolve the residue in dilute hydrochloric acid, add ammonium hydroxide until alkaline, and precipitate with sodium phosphate.

Determination of Alkalies :—For this determination use a special sample. Dissolve in hydrochloric acid, neutralize with ammonium hydroxide, add ammonium carbonate as long as a precipitate is formed and then add yellow ammonium sulphide in slight excess. Warm for some time on the water-bath, and after the precipitate has completely settled, filter, and wash with hot water.

The filtrate contains the alkalies together with the magnesium and some calcium. Decompose the ammonium sulphide with hydrochloric acid, filter, and evaporate the filtrate to dryness. Dissolve the residue in water and separate the magnesium and calcium as given on page 106.

Filter out the precipitate and evaporate the filtrate to dryness in a platinum dish and ignite gently to expel the excess of ammonium oxalate. Moisten the salts with concentrated hydrochloric acid and transfer to an Erlenmeyer flask with absolute alcohol, add an equal volume of anhydrous ether, stopper the flask and allow to digest for at least 24 hours, shaking the contents occasionally*.

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* This method for separating lithium from potassium and sodium, presupposes that the alkalies are present as chlorides. If sulphuric acid is present it must be removed. Barium chloride cannot be used for this purpose, as barium sulphate occludes lithium salts, and the latter cannot be washed out. The sulphuric acid should therefore be removed by lead acetate in boiling solution; cool and add an equal volume of alcohol. Filter off the lead sulphate and remove the slight excess of lead by hydrogen sulphide, after expelling the alcohol. Evaporate the

Decant the ether—alcohol containing the lithium, from the potassium chloride, wash the latter with more ether—alcohol and allow the filtrate and washings to evaporate. The lithium chloride obtained always contains some potassium chloride, which remains undissolved on extracting with alcohol. See analysis of Mineral Water.

Dissolve the lithium chloride in water, add a few drops of concentrated sulphuric acid and determine the lithium as sulphate. See Determination of Potassium as Sulphate, page 106. Gently heat the potassium chloride in a covered platinum crucible and weigh as such. If sodium is present, separate it as given on page 103. The lithium sulphate as well as the potassium chloride should be tested for magnesium.

Determination of Oxygen :—Psilomelane probably contains manganese as MnO_2 together with Mn_2O_3 or MnO. The form, however, cannot be distinguished in the analysis. All the manganese therefore is calculated to MnO, and the amount of oxygen corresponding to Mn_2O_3 or MnO_2 is determined in a separate sample.

Bunsen's method of decomposing the mineral with hydrochloric acid and passing the chlorine into a solution of potassium iodide, is the most accurate. See analysis of Pyrolusite. Liberated Iodine : Oxygen Sought = 253.08 : 15.96. Or, 1 : 0.06036. One part of iodine, therefore, corresponds to 0.06036 parts of oxygen.

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filtrate from the lead sulphate to dryness, with hydrochloric acid, to change the acetates again into chlorides.

According to Jannasch, sulphates may be transformed into chlorides by fusion with 4 to 5 times their weight of boric oxide. Heat until the sulphuric acid is expelled, and then remove the boric oxide with methyl chloride. Compare: Decomposition of Silicates.

Determination of Water :—Proceed as given on page 61. As psilomelane loses its water only at a high temperature, a porcelain tube, instead of a glass tube, should be used.

TIN ORE.

Constituents : Stannic Oxide with small amounts of Ferric Oxide.

As the mineral is not attacked by acids, fuse a weighed amount of the substance dried at 100° C., in a platinum crucible with 8 times its weight of dehydrated sodium thiosulphate, or a mixture of equal parts of sodium carbonate and sulphur.

Allow the fused mass to cool, and extract with warm water ; the tin is in solution as sodium sulpho-stannate, and may be precipitated and determined as given above, page 84.

Ordinarily, a slight black residue of ferrous sulphide is present on extracting with water. Filter it off, wash with water containing hydrogen sulphide and dissolve in hydrochloric acid with a little nitric acid. Precipitate the iron as hydroxide, with ammonium hydroxide.

According to Hampe, tin ore may be dissolved by reducing in a current of hydrogen and then treating with hydrochloric acid. If the mineral contains insoluble silicates, these remain insoluble in the hydrochloric acid. Some tin is volatilized by this treatment, according to the author's experience.*

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* Bongarts and Classen. Determination of the Atomic Weight of Tin. Ber. deutsch. chem. Gesell, Vol. 21. p. 2900.

SPHALERITE.

ZINC BLENDE.

Besides Zinc Sulphide, Sphalerite usually contains appreciable amounts of Lead, Copper, (Arsenic, Antimony), Iron, Manganese, (Cadmium), and Insoluble Matter.

The method for making a complete analysis will be given first, and then the separate determination of zinc will be described.

Finely pulverize the mineral, dry at 100° C., and dissolve about 1 gram in a covered porcelain dish, in fuming nitric acid or aqua regia. First moisten the mineral with water and then add the acid drop by drop between the dish and the edge of the watch-glass. After the acid has acted for some time in the cold, heat on the water-bath or sand-bath until no more red fumes are evolved, and then evaporate to dryness. Add hydrochloric acid to the residue, warm gently, and dilute with warm water. The undissolved gangue may contain crystalline lead chloride, especially if the blend is rich in lead; decant through a filter and dissolve the lead chloride by repeated boiling with water. Ignite, and weigh the insoluble matter.

Determination of Lead :—Add dilute sulphuric acid to the solution, concentrate until all hydrochloric acid is expelled, and determine the lead as given on page 65.

Expel the alcohol by heating, add a little hydrochloric acid and precipitate the copper with hydrogen sulphide. Filter off the cuprous sulphide, wash it first with hydrogen sulphide water containing a little hydrochloric acid, and then with hydrogen sulphide water. Determine the cuprous sulphide as given on page 63.

If cadmium is present, it will be precipitated as cadmium sulphide with the copper. The amount of cadmium present, however, is generally so slight that it is not possible to detect it in 1 gram of the zinc blende. If it is desired to make a quantitative determination, a much larger quantity must be dissolved. To separate cadmium from copper, warm the two sulphides with dilute sulphuric acid (1–5); the cadmium sulphide dissolves and the cuprous sulphide remains insoluble. Filter, wash with water, reprecipitate as cadmium sulphide and determine as such. See: Wood's Metal, page 76.

Vortmann recommends the use of sodium thiosulphate for the separation of cadmium from copper. Add sodium thiosulphate to the acid (preferably sulphuric) solution of the two metals, until the liquid is decolorized, and boil until the sulphur collects together and the supernatant liquid is clear. Filter off the cuprous sulphide, Cu_2S and determine as such.

The cadmium can be precipitated as cadmium sulphide, in the filtrate, and determined as given above.

If the blende contains arsenic and antimony, their determination may be combined with the determination of copper, lead and cadmium. In this case a separate sample should be used.

If the modified Fischer's method (page 91) for separating the arsenic from the other metals is used, after distillation, dilute the residual liquid to the distilling flask with water, precipitate with hydrogen sulphide, and separate the antimony in the precipitate by digesting with a concentrated solution of sodium sulphide. The antimony sulphide is dissolved, and after filtering, may be reprecipitated in the filtrate by the addition of dilute sulphuric acid. Proceed as given on page 79.

The sulphides of copper, lead and cadmium, insoluble in sodium sulphide, can be separated as given above.

Boil the filtrate from the original sulphide precipitate, to expel hydrogen sulphide, and oxidize the iron with nitric acid, hydrogen peroxide or a solution of bromine in hydrochloric acid. Separate the iron from the zinc and manganese, with ammonium hydroxide and ammonium carbonate (page 119.) It should be remembered that the ferric hydroxide always contains an appreciable amount of zinc. Filter and wash the precipitate a few times, dissolve it in hydrochloric acid and repeat the separation*.

Determine the iron by dissolving the precipitate in hydrochloric acid, and titrating with stannous chloride or permanganate. See Volumetric Analysis.

Add acetic or formic acid to the filtrate, and precipitate the zinc as sulphide with hydrogen sulphide. Ignite in a current of hydrogen, and weigh as zinc sulphide.

Separate the manganese in the filtrate as sulphide, with ammonium sulphide, after neutralization with ammonium hydroxide.

Another method of separating manganese from zinc depends upon the precipitation of the former with ammoniacal hydrogen peroxide (Jannasch.) Acidify the filtrate with acetic acid, stir, and add drop by drop to a mixture of equal parts of water, ammonium hydroxide and hydrogen peroxide. Treat the Manganese dioxide as given above†.

The filtrate contains the zinc. Evaporate to dryness and volatilize the ammonium salts by gentle ignition.

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* According to the experiments of Hampe and Fraatz (Zeit. fuer Berg,—Huetten.—und Salienenwesen, 25), and also according to the author's experience, the separation of iron from zinc, by precipitation of the former by ammoniun hydroxide, is not quantitative.

† Results of recent research by Friedheim, show that the method does not give accurate results.

Dissolve in dilute hydrochloric acid, filter out any silica present, and precipitate the zinc as given on page 29.

If the blende contains calcium and magnesium, determine them in the filtrate from the zinc, as given on page 119.

If zinc alone is to be determined in zinc blende, proceed as follows: Finely pulverize the mineral and dry to constant weight. Place about 1 gram in a covered dish, moisten with water to moderate the action of the acid, and then gradually add fuming nitric acid. When the action has ceased, add a little more acid and heat the dish on the sand-bath at a very gentle temperature and warm until no more red fumes are evolved. The temperature should not be high enough to fuse the sulphur as the oxidation then proceeds too slowly. Evaporate to dryness on the water-bath and dissolve the residue in about 15 cc. of dilute sulphuric acid.

Warm, dilute with water, transfer the contents of the dish to a beaker and saturate with hydrogen sulphide. Filter off the sulphide precipitate, wash with hydrogen sulphide water until the filtrate gives no reaction for iron with ammonium hydroxide. Expel the greater part of the hydrogen sulphide by warming on the water-bath, and then oxidize the remainder, together with the ferrous iron, with hydrochloric acid containing bromine.

Evaporate to dryness, dissolve in water and 5 cc. glacial acetic acid and separate the iron and manganese from the zinc by ammoniacal hydrogen peroxide as follows. (Jannasch):

Pour the solution slowly into a mixture of 750 cc. of concentrated ammonium hydroxide and 50 cc of 3 % hydrogen peroxide, while stirring vigorously; cover the dish, and warm for 15 minutes on the water-bath. Filter off the precipitated ferric hydroxide and hydrated manganese dioxide while the solution is hot, and wash with a hot solution of 30 grams ammonium acetate in 75 cc. of strong ammonium hydroxide. With proper manipulation, the separation is complete. If, for any reason, it is necessary to repeat the separation, dissolve the precipitate in a mixture of hydrochloric acid and hydrogen peroxide, and reprecipitate; this time, however, by pouring into a mixture of 10 cc. water, 25–30 cc. ammonium hydroxide, and 15–20 cc. hydrogen peroxide. After destroying the excess of the latter by heating, acidify with acetic acid, and precipitate the zinc with hydrogen sulphide.

Volumetric Determination of Zinc:—Instead of determining the zinc gravimetrically, it is generally determined volumetrically. This method of procedure is especially to be recommended when several determinations have to be made. Numerous methods have been proposed, but only that known to give reliable results will be described.

If a solution of sodium sulphide is added to an ammoniacal zinc solution, a white precipitate of zinc sulphide is produced, as is well known. The end of the reaction is determined by means of paper saturated with lead acetate. Glazed paper, such as is used for visiting cards, is generally used. A glass tube about 25 cm. long and 1 cm. wide, is used to stir the liquid, and may also be used as a pipette for removing a small portion of the liquid for testing.* If a drop of the solution is transferred to the lead acetate paper, a brown ring of lead sulphide is produced if an excess of sodium sulphide is present; the greater the excess of sodium sulphide, the deeper the tint.

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* The titration must be made in a cold solution.

If the liquid being titrated contains a large excess of ammonium hydroxide, there is a reaction between the suspended zinc sulphide and the lead salt of the paper, so that a brown ring would be formed before all the zinc was precipitated. It is therefore necessary to almost completely expel the ammonia, either by heating the solution or allowing it to stand for a long time (18–24 hours), before titrating.

Cobalt paper may be used instead of lead paper. This is prepared by saturating Swedish filter paper with cobalt chloride (.35 grams in 100 cc. water.) An excess of sodium sulphide produces a sharply defined black spot, when a drop of the solution is placed on the cobalt paper.

To obtain closely agreeing results, it is necessary to take the same tint as the end reaction in both the actual titration and in standardizing the sodium sulphide solution. The same degree of dilution should be used in both cases.

In preparing the sodium sulphide solution, use the crystallized sulphide, Na_2S+9H_2O, and dilute so that 1 cc. corresponds to about .005 gram zinc.

The strength of this solution is determined with C. P. zinc. As above mentioned, the same conditions must be observed in standardizing the solution and in the actual analysis. If, for example, 1 gram of ore, containing about 50% zinc is to be titrated, about 50 grams of pure zinc should be used in standardizing the sodium sulphide solution, and the dilution in the two cases should be about the same.

In the laboratories of some of the German zinc works, the following method is used: Dissolve 0.5 gram of sphalerite in warm hydrochloric acid with the addition of some nitric acid. Evaporate off the acid and dissolve the residue in a definite amount (about 10 cc.) of hydrochloric acid. Precipitate the lead, copper, etc., with hydrogen sulphide, and filter.

Expel the excess of hydrogen sulphide by boiling, oxidize the solution with nitric acid (about 5 cc.) and add about 20 cc. of bromine water and 20 cc. ammonium hydroxide to oxidize the manganese. Filter off the precipitate of ferric hydroxide, etc., wash it a few times with hot water, dissolve in 10 cc. hydrochloric acid, and repeat the precipitation with 15 cc. ammonium hydroxide. Filter, and wash with hot water. Unite the filtrates, dilute to a definite volume, allow to stand 18–24 hours, and then titrate with sodium sulphide. The sodium sulphide is standardized as given above, using the same concentration in both cases, with the additional refinement of adding the same amounts of hydrochloric and nitric acids, bromine water and ammonium hydroxide, in both cases.

Determination of Sulphur:—Sphalerite may be oxidized with fuming nitric acid*, if the precaution is taken to allow the acid to act for some time before warming. It is convenient to proceed as follows: Moisten about 0.5 gram of the finely ground mineral with water in a covered porcelain dish, add fuming nitric acid drop by drop, until no further action is visible. After standing for 1–2 hours, warm gently on the sand-bath or water-bath as long as oxides of nitrogen are evolved. Now slowly add hydrochloric acid, warm, and evaporate to dryness. Warm the residue with dilute hydrochloric acid, filter, and wash the insoluble matter, first with small amounts of hot dilute hydrochloric acid and then with hot water. Dilute, and precipitate the sulphuric acid with barium chloride as usual.

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* For other methods of determining sulphur in sulphides, see analysis of Pyrites.

CALAMINE AND ZINC SILICATES.

Constituents: Zinc, (Cadmium) Copper, Lead (Arsenic, Antimony), Iron, Manganese, Calcium, Magnesium, Carbon Dioxide, Silica and Water.

The analysis can be made as in the case of Sphalerite. If it is desired to separate silica from sand or insoluble matter, proceed as given on page 127.

As carbon dioxide is completely expelled from calamine by ignition, the determination of the latter may be united with the determination of water. Weigh out 1–2 grams of the mineral in a porcelain boat, place in a tube of difficultly fusible glass and connect the tube with a previously weighed calcium-chloride tube and the latter with a weighed U-tube filled with soda lime. After strongly igniting the substance, the gain in weight of the tubes gives the weight of water and carbon dioxide, respectively.

PHOSPHORITE.*

Principal Constituents: Calcium Phosphate, with Calcium Chloride, Calcium Fluoride (Calcium Iodide), and small amounts of Iron, (Manganese), Aluminum, (Magnesium), Alkalies, and Water.

If the phosphorite is free from ferric oxide, alumina and magnesia, dissolve about 0,5 gram in fuming hydrochloric acid, filter off the insoluble matter, and concentrate by evaporation, until the residue appears just moist; add a few drops of dilute hydrochloric acid and 3–4 grams of potassium oxalate solution (1–3.) When the calcium oxalate has settled, filter, wash with hot water until a few drops of the filtrate leaves no residue when evaporated on platinum foil. Determine the calcium as oxide. If the phosphorite contains manganese, it is precipitated as oxalate with the calcium.* The ignited calcium oxide is then colored more or less brown by Mn_2O_3. The latter may be determined by weighing the two oxides together and then determining the manganese volumetrically.†

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* [This natural fertilizer includes the vitreous, earthy, scaly and fibrous forms of Apatite. While Phosphorite is not found in the United States, the same method serves for the analysis of Apatite.

Precipitate the phosphoric acid in the filtrate from the calcium oxalate with magnesium chloride solution, after supersaturating with ammonium hydroxide. Before the other bases can be determined, the phosphoric acid must be separated. Dissolve a sample of the phosphorite in hydrochloric acid, filter off the silica, evaporate the excess of acid, add concentrated nitric acid, and evaporate again. Repeat the evaporation with nitric acid 5 or 6 times, to form nitrates. Pour fuming nitric acid on the residue, add 5–8 times as much metallic tin as there is phosphoric acid present, and warm the covered dish on the water-bath until all the tin is oxidized. All phosphoric acid is changed into stannic phosphate which is insoluble in

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* Classen, Zeit. f. anal. Chem., Vol. 16, p. 318.

† Boil the precipitate with hydrochloric acid in Bunsen's apparatus, pass the liberated chlorine into a solution of potassium iodide, and titrate the liberated iodine with sodium thiosulphate. See Volumetric Analysis; Sodium Thiosulphate and Iodine.

$$Mn_2O_3 + 6HCl = 2Cl + 2MnCl_2 + 3H_2O$$
$$2KI + 2Cl = 2KCl + 2I.$$
$$2I = Mn_2O_3\,.$$

nitric acid. Allow the precipitate of stannic phosphate and stannic oxide to settle, dilute with water, filter, and wash the precipitate by decantation with water containing nitric acid*. Evaporate the filtrate to dryness. As tin ordinarily contains copper, pass hydrogen sulphide through the hydrochloric acid solution of the residue, oxidize the filtrate, and precipitate the iron and aluminum as hydroxides with ammonium hydroxide. Determine the calcium and magnesium in the filtrate, as given on page 119.

To determine the alkalies, precipitate the hydrochloric acid solution of the phosphorite, with ammonium hydroxide, filter off the precipitate, wash it with hot water, acidify the filtrate with hydrochloric acid and evaporate to dryness.

After volatilizing the ammonium salts by gentle ignition, separate the magnesia and determine the alkalies as given on page 105.

Determination of Fluorine :—The direct determination of this element in the presence of phosphoric acid in compounds insoluble in water, is somewhat difficult. Therefore the calcium fluoride is generally calculated by difference. The phosphoric acid and chlorine being combined with part of the calcium, and the remainder assumed to be calcium fluoride. Fluorine may be determined directly, in the following manner: Mix the finely pulverized substance with silica (preferably, silica separated from silicates) and potassium carbonate, and fuse at a low red heat†. The water solution of the fused mass contains all the fluorine in the form of potassium fluoride, together with potassium phosphate and potassium silicate. First separate the phosphoric acid by means of silver nitrate. Filter out the silver phosphate, wash it with a small amount of water, and precipitate the excess of silver nitrate with sodium chloride. To separate the silica still in solution, from the flourine, add ammonium carbonate, warm for some time on the water-bath, filter, and evaporate the filtrate to dryness. The residue still contains a small amount of silica, together with all the fluorine as potassium fluoride. Dissolve the residue in hot water, add sodium carbonate and a slight excess of a solution of zinc oxide in ammonium hydroxide, and evaporate on the water-bath until the odor of ammonia cannot be detected. Filter off the zinc silicate, wash it with water, and precipitate the fluorine in the filtrate as calcium fluoride. For this purpose, transfer the solution to a platinum or porcelain dish, heat to boiling, add a solution of calcium chloride and continue the boiling for some time.

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* The precipitate should be digested with ammonium sulphide to separate traces of iron and aluminum. Filter, acidify the filtrate with hydrochloric acid, oxidize, and add to the main solution.

† The temperature should not be too high, as potassium fluoride may be volatilized.

Do not filter until the liquid appears perfectly clear. Wash the precipitate by decantation, with hot water. It is best to decant off the clear solution, add hot water and boil for a few minutes, and decant again. Repeat this operation until the precipitate is sufficiently washed, then transfer the precipitate to the filter.

The precipitate produced by calcium chloride is a mixture of calcium fluoride and calcium carbonate, (from the sodium carbonate.) The latter may be separated from the calcium fluoride by igniting the residue in a platinum dish and adding acetic acid, after cooling. Evaporate to dryness on the water-bath, and remove the calcium acetate by washing with hot water. Ignite and weigh the pure calcium fluoride, CaF_2.

Offermann has based a volumetric method for the determination of fluorine on the volatilization of fluorine as silicon tetrafluoride, decomposition of the latter by water, and formation of fluosilicic acid; the fluosilicic acid is then titrated with normal alkali solution:

$$H_2SiF_6 + 6KOH = 6KF + Si(OH)_4 + 2H_2O.$$

This method is also applicable in the presence of carbonates, chlorine and organic substances. Fig. 29 shows the arrangement of the apparatus.

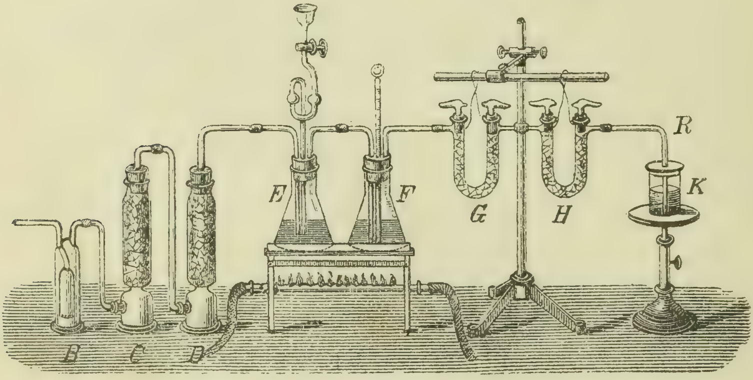

Fig. 29.

The wash bottle B, which is connected with a gasometer filled with air, contains concentrated sulphuric acid. The two drying towers C and D, are one-half filled with granular soda-lime, and the other half with granular calcium chloride. The flask E, holding 200–250 cc., serves for the decomposition of the fluoride. F contains concentrated sulphuric acid. A thermometer is inserted through one hole of the stopper, so as to observe the temperature; E and F stand on an iron or asbestos plate. G and H serve to remove the last traces of water and hydrochloric acid ; they are filled with granular calcium chloride and dehydrated copper sulphate.

The bottom of the beaker K is covered with a layer of mercury, in which the tube R is slightly immersed. The water above the mercury serves to decompose the silicon tetrafluoride.

Mix the weighed mineral with 15 times its weight of quartz sand, transfer the mixture to E, connect E with F and add 50 cc. of concentrated sulphuric acid through the funnel tube. Pass a slow current of air (1–2 bubbles per sec.) from the gasometer through the apparatus, gradually heat E and F and increase the temperature to 150° C. When no more bubbles of gas are formed in E, the decomposition is ended. Allow the apparatus to cool while passing a slow current of air, and then titrate the fluosilicic acid in K, with standard potassium hydroxide. See Volumetric Analysis.

6 molecules of sodium hydroxide correspond to 1 molecule of fluosilicic acid ; 1 cc. of normal potassium hydroxide therefore corresponds to 0.019 gram of fluorine,

During the decomposition, silica is deposited in the tube in K ; this should be removed occasionally with a platinum wire.

Gasometric Determination of Fluorine, (Hempel) :— In this method, the fluorine is volatilized in the form of silicon tetrafluoride and the volume of the gas measured in a gas burette. Since many substances which contain fluorine also contain carbon dioxide, the method provides for the possible presence of this constituent.

The operations are as follows : Decompose the substance by sulphuric acid in the presence of silica, in a perfectly dry apparatus, and measure the resulting mixture of gases, consisting of air, carbon dioxide and silicon tetrafluoride. After the silicon tetrafluoride has been decomposed by shaking up with water, the resulting gas volume is measured, and the contraction shows the amount of silicon tetrafluoride present. However, as the carbon dioxide is at least partly absorbed by the water, the observed volume of silicon tetrafluoride is too great, and must be corrected by a subsequent determination of the absorbed carbon dioxide.

Remove the carbon dioxide from the residual gas mixture, by means of potassium hydroxide, and determine its volume by difference.

To determine the carbon dioxide that was absorbed with the silicon tetrafluoride in the water, bring the remaining gas (consisting of air) again in contact with the water containing the carbon dioxide, and agitate ; this liberates the carbon dioxide from the water. By again shaking the gas with potassium hydroxide, the carbon dioxide may all be absorbed, and its volume then subtracted from the volume of silicon tetrafluoride, thus obtaining the true volume of the latter gas.

The substances required are, finely pulverized quartz, freed from organic substances by long ignition in the air, and concentrated sulphuric acid, which should be mixed with about 5 grams of flowers of sulphur and evaporated to 2/3 its original volume to free it from organic matter and oxides of nitrogen.

The apparatus, Fig. 30, consists of the decomposing flask A, in the neck of which a condenser is connected by a ground glass joint. A side tube from the decomposing flask, is provided with a plug which is likewise connected with a ground-glass joint, and is provided with a stopcock, h.

The figure shows how the joints are sealed by the liquid. The upper end of the condenser is provided by a capillary tube and is connected with the gas burette B by means of a dry rubber tube, which may be closed at will by a pinch-cock. The burette is provided with a glass stop-cock near its foot, and is connected with the levelling bulb C by means of a long rubber tube.

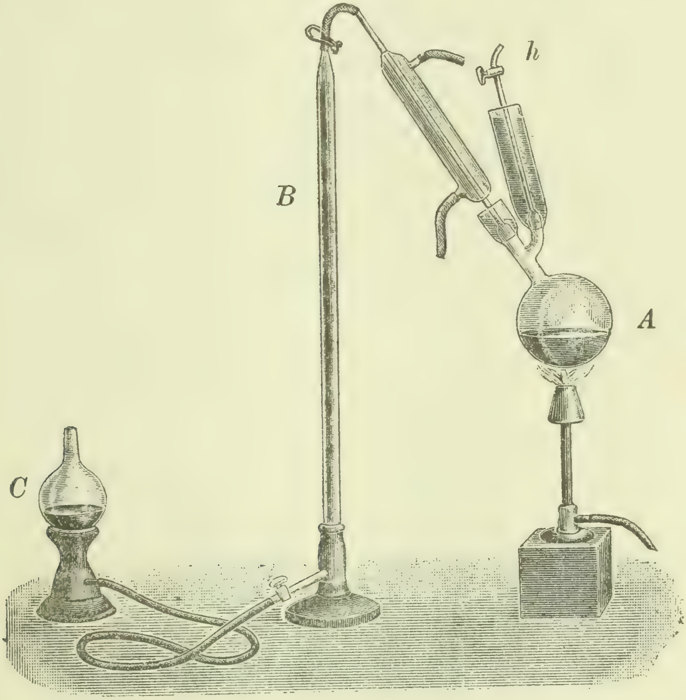

Fig. 30.

Pour .25–.5 cc. of concentrated sulphuric acid into the burette to be sure that all traces of water are removed, as it would decompose the silicon tetrafluoride. Now fill the burette and the levelling bulb to the zero point with mercury, and close the lower stop-cock. Place the substance containing fluorine, and the quartz powder, in the flask A which should be perfectly dry, and thoroughly mix by shaking. Connect the flask with the burette by means of the condenser, and seal the joints with concentrated sulphuric acid. Connect the tube h with the vacuum pump, exhaust the air from the apparatus, and close the stopcock in h. Now carefully remove the tube h and allow the greater part of the acid to suck into the flask, and heat to boiling.

Remove the flame, open the cock at the foot of the burette, and fill the flask A, and the condenser with concentrated sulphuric acid through the side tube, by carefully lifting the tube h. All the gas is thus driven over into the measuring burette. After the apparatus has assumed the temperature of the room, bring the gas under atmosphere pressure by means of the levelling bulb C,

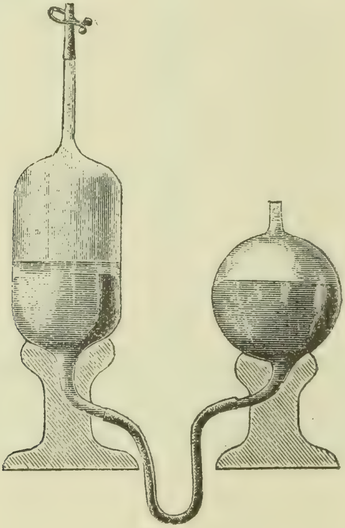

Fig. 31.

Note the barometric pressure, the temperature of the air near the apparatus and the volume of the gas.

If sufficient gas should not be evolved, allow air to enter, by lowering the bulb C and then opening the stopcocks, until the total volume is about 110 cc. Close the burette above and below, and proceed to absorb the gas. For this purpose, the absorption pipette, shown in Fig. 31, is used first. The cylindrical part of the apparatus is about half full of mercury, on the surface of which is a layer of about 5 cc. of water. The apparatus is placed on a stand so that it may conveniently be connected with the burette by means of a capillary tube. Force the water up to the top of the absorption bulb, by raising the levelling bulb, connect the latter with the burette, and then transfer the gas to the absorption bulb, by raising the levelling bulb C, and lowering the bulb of the absorption pipette.

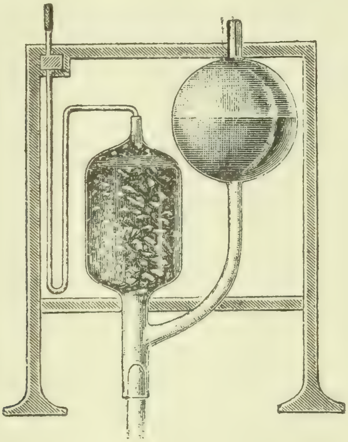

Fig. 32.

When the gas is all transferred, close the absorption pipette with the pinch-cock, agitate for 5 minutes, and then return the gas to the measuring burette, and measure the volume. The contraction corresponds to the volume of the silicon tetrafluoride plus a small amount of carbon dioxide*. See above. Now transfer the gas to an absorption pipette, Fig. 32, filled with glass beads and concentrated potassium hydroxide (1–200), agitate as before and return to the measuring burette and note the contraction. Transfer the gas once more to the pipette used at first containing water and mercury, agitate about 3 minutes and again measure the volume. After the gas has been agitated in contact with potassium hydroxide once more, the final volume is measured. The difference between the last two measurements, gives the slight amount of carbon dioxide which was absorbed with the silicon tetrafluoride by the water. This small amount subtracted from the first contraction, gives the volume of silicon tetrafluoride in the gas mixture.

Determination of Chlorine:—The chlorine is determined as silver chloride in nitric acid solution of about 5 grams of the Phosphorite. It should be remembered that hydrochloric acid may be volatilized, if the nitric acid solution is heated strongly, or if the solution is allowed to concentrate during solution.

Determination of Iodine.—Many Phosphorites contain a small amount of calcium iodide. To determine the iodine, heat about 100 grams of the substance in a retort of about 500 cc. capacity, with about 100 cc. of concentrated sulphuric acid and pass the vapor into dilute potassium hydroxide. After boiling the contents of the retort for about half an hour, all the iodine will be in the distillate. Acidify the latter with dilute hydrochloric acid, and precipitate the iodine as palladous iodide PdI_2, with palladium chloride or nitrate. See page 44. The iodine may also be determined volumetrically in the distillate, after acidifying with hydrochloric acid.

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* If sulphuric acid liberates hydrochloric acid from the substance, the latter is likewise absorbed by water. In this case, determine the hydrochloric acid in the usual manner, calculate the volume and subtract it from the volume of silicon tetrafluoride found.

For this purpose, add some potassium bichromate and titrate the liberated iodine with thiosulphate. See: Volumetric Analysis, Sodium Thiosulphate and Iodine.

Determination of Phosphoric Acid:—In the valuation of Phosphorites, a determination of phosphoric acid is generally sufficient. If the phosphorite contains ferric oxide, etc., it is preferable to determine the phosphoric acid in a special sample, either gravimetrically or volumetrically.

Gravimetric Determination of Phosphoric Acid:—Dissolve 0.3 0.5 gram of the substance by digesting with fuming hydrochloric acid. When decomposition is effected, evaporate to dryness. Moisten with nitric acid and repeat the evaporation. Add a little nitric acid, warm, and then dissolve in water. Filter, if necessary, and precipitate the phosphoric acid with ammonium molybdate, as given on page 42. Determine as Magnesium Pyrophosphate.*

Volumetric Determination of Phosphoric Acid:—The phosphoric acid can be determined almost as accurately volumetrically, and the following method has been considerably used in practice. The method is based upon the precipitation of phosphoric acid by uranium acetate in acetic acid solution. Potassium ferrocyanide is used as an indicator to show when all the phosphoric acid has been changed to uranyl phosphate.

The details of this method are given under Volumetric Analysis.

Dissolve the phosphorite in fuming hydrochloric acid,† or in 5% sulphuric acid. If hydrochloric acid is used, remove the excess by evaporating nearly to dryness, so that on dilution with water, a clear solution results.

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* [The ammonium phospho-molybdate may also be dissolved in an excess of standard potassium hydroxide, and the excess titrated back with standard nitric acid. See: Determination of Phosphorus in Steel, etc.]

† It is preferable to use 5 per cent. sulphuric acid in the determination of phosphoric acid in phosphorites which contains a considerable quantity of iron or alumina. Filter off the insoluble residue of calcium sulphate, silica, ferric oxide, etc., wash it with hot water, make alkaline with ammonium or sodium hydroxide, and then add acetic acid to acid reaction.

Neutralize the remainder of the acid with ammonium hydroxide, avoiding an excess, and dissolve the resulting precipitate in acetic acid. Now add 10 cc. of sodium acetate, dilute to the same volume used in standardizing the uranium acetate solution, and proceed as given under this method in Volumetric Analysis.

If the results are to be comparable with the results of gravimetric analysis, it is necessary to observe the same conditions of dilution, etc., in the actual analysis and in standardizing the uranium solution. Otherwise the action of the latter solution is not definite. As these conditions cannot always be observed, the constancy of the action of the uranium solution within definite limits, must be considered, if exact determinations are to be obtained. Brookmann has given a correction table which gives the value of the uranium solution from 20 to 40 cc. This table has been made more complete by A. Haswell, by adding the values from 1.2–20 cc.

Brookmann used a flask provided with a mark at a volume of 130 cc. and used a solution which contained 0.35 gram of potassium ferrocyanide in 4.5 cc. of water, as an indicator. According to this investigator, at the above dilution (130 cc.), and in the presence of 12.5 cc. of a solution of sodium acetate (see Volumetric Analysis), 0.55 cc. of uranium acetate solution (1 cc. = 0.005 gram P_2O_5) are required to give the end reaction in the absence of phosphoric action. The table gives the influence of this amount of the solution, from 2–40 cc. The uranium solution has the following values:

cc.	of uranium	solution	used;	1 cc.	corresponds to	grams P_2O_5
1.2	“	“	“	“	“	.004167
2.3	“	“	“	“	“	.004347
3.3	“	“	“	“	“	.004544
4.2	“	“	“	“	“	.004762
5.1	“	“	“	“	“	.004901
6-1	“	“	“	“	“	.004918
7.1	“	“	“	“	“	.004928
8.1	“	“	“	“	“	.004938
9.1	“	“	“	“	“	.004945
10.1	“	“	“	“	“	.004950
11.1	“	“	“	“	“	.004954
12.1	“	“	“	“	“	.004958
13.1	“	“	“	“	“	.004962
14.1	“	“	“	“	“	.004964
15.1	“	“	“	“	“	.004967
16.1	“	“	“	“	“	.004968
17.1	“	“	“	“	“	.004985
18.0	“	“	“	“	“	.00500
19.0	“	“	“	“	“	.00500
20.0	“	“	“	“	“	.00500
22.0	“	“	“	“	“	.00502
23.0	“	“	“	“	“	.00504
24.0	“	“	“	“	“	.00505
25.0	“	“	“	“	“	.00506
26.0	“	“	“	“	“	.00507
27.0	“	“	“	“	“	.00508
28.0	“	“	“	“	“	.005085
29.0	“	“	“	“	“	.00509
30.0	“	“	“	“	“	.005095
31.0	“	“	“	“	“	.0051
32.0	“	“	“	“	“	.005105
33.0	“	“	“	“	“	.00511
34.0	“	“	“	“	“	.005115
35.0	“	“	“	“	“	.00512
36.0	“	“	“	“	“	.005125
37.0	“	“	“	“	“	.00513
38.0	“	“	“	“	“	.005135
39.0	“	“	“	“	“	.00514
40.0	“	“	“	“	“	.00514

VANADINITE.

Constituents: Lead Vanadate and Lead Chloride; commonly contains Phosphoric Acid, and occasionally Arsenic Acid.

Determination of Chlorine and Lead:—Dissolve about 1 gram of the finely pulverized mineral in dilute nitric acid without warming, as otherwise chlorine may be expelled. Dilute, and precipitate the chlorine with silver nitrate. After removing the excess of silver nitrate in the filtrate with hydrochloric acid, evaporate the silver-free filtrate to dryness several times after adding hydrochloric acid, to expel the nitric acid. Add alcohol and determine the lead chloride as given on page 43.

Determination of Vanadium:—The preceding treatment reduces the vanadic acid to the vanadyl condition, as is shown by the blue color of the solution. Repeated evaporation with nitric acid oxidizes the lower oxide to the brown pentoxide again. Transfer to a weighed platinum crucible with as little water as possible, dissolve the particles adhering to the dish with a little ammonium hydroxide, transfer to the crucible and evaporate to dryness. A residue of ammonium vanadate is thus obtained. Heat gradually to expel the ammonia and then ignite with access of air until the dark colored, lower oxides formed by the reducing action of the ammonia, are again oxidized to the ocher-colored pentoxide. Increase the temperature until the latter fuses; on cooling, the mass forms a radiated, crystalline mass. Weigh as V_2O_5.

If the vanadinite contains phosphoric acid, the latter will be with the vanadic acid; in this case, the mass commonly sinters together instead of fusing. Fuse the weighed residue with an equal weight of sodium carbonate, dissolve the fuse in water, acidify with sulphuric acid, add sulphurous acid and boil. This reduces the vanadium pentoxide to tetroxide.

Expel the excess of sulphur dioxide to avoid a reduction of the molybdic acid which is to be added later. Add a few drops of nitric acid, a little ammonium nitrate, and then a large excess of ammonium molybdate solution. As the vanadium tetroxide on long standing, is again oxidized to pentoxide by the nitric acid of the ammonium molybdate, and passes in part into the phospho-molybdate precipitate, the solution is warmed for only a short time at 60° C. and then cooled and filtered at once. Determine the phosphoric acid as given on page 41, and subtract its weight from the weight of the mixed oxides, and obtain the vanadium pentoxide by difference.

It is best to use a separate sample for the determination of arsenic acid. Use the distillation method described on page 91, *et seq.*

According to Friedheim, the vanadic acid may be determined volumetrically. As vanadium pentoxide is not reduced to a definite state of oxidation by hydrochloric acid, the reduction is effected by hydrobromic acid, according to the following equation :

$$V_2O_5 + 2HBr = V_2O_4 + H_2O + Br_2.$$

1 mol. of liberated bromine thus corresponds to 1 mol. of vanadium pentoxide. By passing the bromine into a solution of potassium iodide, an equivalent amount of iodine is liberated :

$$2KI + Br_2 = 2KBr + I_2.$$

Titrate the iodine with thiosulphate. If 1 cc. of the latter corresponds to a grams of iodine, and if t cc. of thiosulphate were used, the amount of vanadium pentoxide in the sample taken is given by the proportion :

$$I_2 \; ; \; V_2O_5 = at : X,$$

$$\text{From which, } X = \frac{V_2O_5}{I_2} \, at.$$

The distillation is made in Bunsen's apparatus, exactly as described under the Standardization of Sodium Thiosulphate. See Volumetric Analysis. Place about 0.1–0.2 gram of the mineral, and 0.5–1.0 gram of potassium bromide in the distillation flask, add strong hydrochloric acid and boil until the green solution has assumed a pure blue color.

ULEXITE.

Constituents : Calcium, Sodium, Boric Acid and Water. The mineral often contains Potassium Chloride, Sodium Chloride, and Sodium Sulphate.

Determination of the Non-Alkaline Bases :—Before determining these constituents, it is necessary to volatilize the boric acid. Add hydrofluoric acid to a weighed amount of the substance and digest for some time on the water-bath. After cooling, carefully add concentrated sulphuric acid drop by drop, and heat until the excess of acid is expelled ; this volatilizes all the boric acid as boron fluoride and leaves the metals as sulphates.

Ammonium fluoride may be used instead of hydrofluoric acid. Intimately mix the mineral and the salt, add concentrated sulphuric acid and heat gradually.

Dissolve the sulphates in hydrochloric acid, neutralize the solution with ammonium hydroxide and separate the calcium as oxalate.

The alkalies may be determined in the filtrate from the calcium oxalate. Evaporate to dryness, and weigh the alkalies as sulphates. It should be remembered that a little ammonium carbonate should be added before the final ignition, to decompose the acid sulphates. See page 106.

Separate the sodium and potassium as given on page 104.

Determine the hydrochloric and sulphuric acids as usual, in nitric and hydrochloric acid solutions, respectively.

Determination of Boric Acid as Potassium Fluoborate.

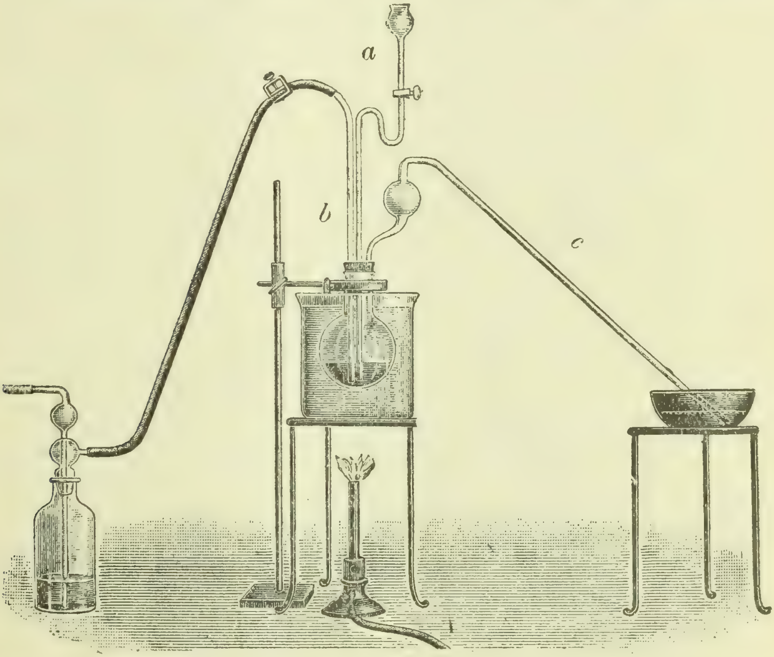

Fig. 23.

Berzelius-Stromeyer Method, modified by Thaddeeff:—This method depends upon the insolubility of potassium fluoborate in a definite mixture of potassium acetate and alcohol. The method presupposes that only boric acid or its potassium salt is present in the solution to be precipitated, as the salts of other bases or acids would be precipitated with the potassium fluoborate in alcoholic solution. This requires that the boric acid be expelled from its compounds and then combined with potassium. For this purpose, the borate is distilled with sulphuric acid and methyl alcohol, and the easily volatile boric ether absorbed in pure potassium hydroxide. The apparatus is shown in Fig. 33.

Place the weighed substance in the flask, which should have a capacity of about 80–100 cc., and support it by means of a retort-stand in a beaker which serves for a water-bath. The beaker should be covered with a copper plate to prevent loss of water by evaporation. The flask is closed with a 3-hole rubber stopper, provided with 3 tubes, a, b and c; a and b reach to the bottom of the flask. The tube b, which is drawn out to a narrow opening at its lower end, serves for passing a current of air from a gasometer. The rate of flow of the air can be regulated by the screw pinch-cock. The air is passed through a wash bottle filled with potassium hydroxide to remove carbon dioxide, and then through concentrated sulphuric acid to remove water vapor. The exit tube c, is drawn down to a narrow opening at its lower end and is immersed in a platinum dish containing 3 grams of pure potassium hydroxide in 200 cc. of water. The dish should be covered with a watch-glass.

Close the pinch-cock, pour through the funnel a cooled mixture of 10 cc. of methyl alcohol, and 2–3 cc. of sulphuric acid, Sp. Gr. 1.84, add 10 cc. more of methyl alcohol and close the stop-cock in the funnel; now begin the distillation by warming the water-bath.

To save time, hot water may be poured into the beaker, after everything is in readiness. As soon as two-thirds of the liquid has distilled over, pass a current of air through the apparatus for about 5 minutes.

Now add 10 cc. more of methyl alcohol. If, to save time, the alcohol is added to the hot acid, the greatest care must be observed, as the reaction is quite violent. There is, in fact, a double danger in so doing; first, the sucking back of the potassium hydroxide as a result of the cooling of the air in the apparatus by the sudden evaporation of the alcohol, and second, the spirting in the platinum dish, in consequence of the violent boiling.

By suitably regulating the current of air, both dangers may be avoided.

After distilling for 5–10 minutes without passing the air, open the stop-cock and pass a slow current of air for 10–15 minutes, add 10 cc. more of methyl alcohol, distil for 5–10 minutes without access of air, and finally pass a slow current of air for half an hour, at first warming the flask and then gradually allowing it to cool. Finally remove the water-bath.

After the boric acid has been combined with the potassium, the precipitation is made as follows:

Evaporate the contents of the dish on the water-bath, to half its volume, add an excess of C. P. hydrofluoric acid, and evaporate as much as possible on the water-bath, occasionally breaking the crust of salt that forms. When the residue smells only faintly of hydrofluoric acid, (a very small amount of acid is neither advantageous nor harmful), allow to cool, add 50 cc. of a clear potassium acetate solution, Sp. Gr. 1.14, stir occasionally with a platinum wire, and allow to stand 1–2 hours at the ordinary temperature.

The large pieces of salt should be crushed, to facilitate solution of the potassium fluoride. When all soluble matter is in solution, add 10 cc. of alcohol, Sp. Gr. .805, stir carefully and allow to stand for 12–14 hours.

In the meantime, moisten a 9 cm. filter with alcohol, dry for 3 hours at 100–110° C. in a weighing bottle, and cool in a dessicator containing fresh calcium chloride.

It is necessary to moisten the filter with alcohol before drying and weighing, as the precipitate is finally washed with alcohol, and the weight of the filter is increased 1 or 2 milligrams.

Transfer the precipitate to the filter with alcohol, Sp. Gr. .805, and rinse out the dish 4–5 times with alcohol.

It is advisable to use a ribbed funnel for the filtration. After washing the precipitate with alcohol, dry it at 100–110° C. in the same manner in which the filter was treated.

As mentioned above, the solution to be precipitated should contain no acid other than the boric acid. If, however, ulexite is subjected to the above distillation, hydrochloric acid is distilled over, and the potassium fluoborate is contaminated with potassium chloride, which is also insoluble in alcohol. To determine the potassium chloride, extract the weighed precipitate with potassium acetate, in which the potassium chloride is soluble while the potassium fluoborate is almost entirely insoluble ; determine the chlorine in the extract, and subtract an equivalent amount of potassium chloride from the weight of the mixed precipitate.

The water is best determined by mixing a weighed quantity of the mineral, with a weighed quantity of freshly ignited lead oxide, and heating in a tube of hard glass.

BORACITE.

Contains: Magnesium Borate and Magnesium Chloride.

To separate the magnesium from the boric acid, fuse the mineral with 4 times its weight of potassium carbonate, and digest with water. After filtering out the insoluble residue and washing it with hot water, it may be ignited and weighed as magnesium oxide, or dissolved and precipitated as magnesium-ammonium phosphate.

Determine the boric acid in the filtrate, in which it is present as the potassium salt, according to the method given on page 167. As the filtrate contains chlorine, the precaution mentioned above should be observed.

Determine the chlorine in a special sample, by dissolving in nitric acid, and precipitating as silver chloride, as usual.

If the boracite contains water (Massive Boracite), it may be determined as given under Ulexite.

ANALYSIS OF SILICATES.

Silicates may be divided into two groups, according to their behavior towards acids: Silicates Decomposable by Acids, and Silicates not Decomposable by Acids.

The first group contains, for example:

Allanite, Allophane, Analcite, Botryolite, Brewsterite, Calamine, Chabasite, Cronstedtite, Datolite, Dioptase, Eulytite, Gadolinite, Gahlenite, Helvite, Ilvaite, Melinite, Natrolite, Nephelite, Okenite, Pectolite, Wernerite and the Zeolites.

Among the silicates not decomposable by acids, may be mentioned:

Albite, Andalusite, Augite, Axinite, Beryl, Carpholite, Cyanite, Diallage, Euclase, Feldspar, Garnet, Iolite, Labradorite, Potassium and Magnesium Micas, Oligoclase, Petalite, Pinite, Prochlorite, Pumice, Serpentine, Sillimanite, Talc, Tourmaline, Vesuvianite, etc.

Determination of Silica in Silicates Decomposable by Acids.

Hydrochloric acid is generally used for the decomposition; more rarely nitric acid, as for example, in the case of silicates containing lead or silver; concentrated sulphuric acid is sometimes used, especially in decomposing aluminum silicates. Before proceeding to the analysis proper, it is necessary to pulverize the silicate as finely as possible and then to dry the powder.

Ordinarily the drying can be done by heating the sample in the air-bath at 100° C. If, however, the silicate loses combined water at this temperature, the drying must be done at a lower temperature, or even over sulphuric acid.

The method used in determining the water must be varied according to the nature of the silicate. If the substance, on ignition, loses all its water without losing carbon dioxide or organic matter, or absorbing oxygen, as in silicates containing ferrous oxide, the simplest method is 'loss on ignition.'

In other cases, the direct determination, as given under Dolomite, page 61, must be used.

The water may also be determined by placing the sample in an open tube between plugs of asbestos or glass wool, and heating, while aspirating a slow current of air freed from moisture and carbon dioxide. If the sample evolves but small amounts of these constituents, they may be absorbed in U-tubes containing calcium chloride and soda lime.

Silicates, like tourmaline, which give off their water only when heated to a very high temperature, are decomposed more easily by fusing with dehydrated borax (Jannasch). Mix .5–.1 gram of the finely pulverized substance with 1.5 grams of completely dehydrated borax, in a large platinum boat, transfer to a glass tube, and heat in a current of air until in quiet fusion. If the substance evolves fluorine on being heated, it may be absorbed by a layer of dry, granular lead chromate 7–8 cm. in length, or by previously fused lead oxide.

Minerals like topaz, which contain a large amount of fluorine, may be fused with 6 times their weight of pure lead oxide in a bulb tube of difficultly fusible glass. The vapors should be passed through a layer of lead oxide in one end of the tube, to absorb fluorine, and the water may be carried over into a calcium chloride tube by a current of air*.

In determining water in a silicate, it may be of interest to ascertain in what form the water is contained in it. Many silicates contain water of crystallization (Krystallwasser). Among these, are the Zeolites: Analcite, Apophyllite, Chabasite, Phillipsite, Harmotome, Heulandite, Natrolite, Scolecite, and Stilbite. As this water is given off at a low temperature, and even in a dessicator, care should be taken that no loss occurs on drying the sample. Such samples should be dried in a dessicator over sand that has previously been dried at 200° C†.

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* [Compare: W. F. Hillebrand, Bull, 176, U. S. Geol. Surv., p. 46.]

† [“ “ “ “ “ “ “ “ “ “ “ 33.]

The samples should then be dried to constant weight in the air-bath at the successive temperatures, 100°, 125°, 150° C., etc. All water given off below 360° C, is assumed to be water of crystallization.

All water expelled by heating from 360° C. up to the temperature of ignition, is assumed to be water of constitution.

Place a weighed portion of the dried powder in a platinum or porcelain dish, moisten all over with water so that a thick paste is formed, add hydrochloric acid, and warm on the water-bath while stirring with a platinum spatula. The silica generally separates in a gelatinous form, and it is easy to ascertain when all the hard particles are decomposed. It should not be forgotten that if undecomposable silicates or quartz are present, the gritty feel may be due to these.

In decomposing a mineral with hydrochloric acid, the most of the silicic acid separates in the insoluble form, and the remainder remains in solution. Some silicates, however, may dissolve to a clear solution in hydrochloric acid. In all cases, evaporate the solution to dryness and heat the residue in an air-bath until the odor of hydrochloric acid is gone, and the salts are perfectly dry. This renders the silica insoluble. If the silica contains neither iron nor alumina, the dried mass may be heated for some time in an air-bath at 120° C.

In either case, moisten the cooled mass with hydrochloric acid, and warm about half an hour to dissolve the basic salts formed by the dehydration. Now add hot water, stir for a few minutes and filter. As the silica clogs the pores of the filter, it is advisable to wash by decantation and then to transfer the silica to the filter by means of the wash bottle.

The filtrate contains the bases together with a very small amount of silica, even if the drying was done at 120° C. In exact analysis, therefore, the filtrate must be evaporated to dryness and dehydrated a second time.

Dry, ignite and weigh the silica. Wrap the precipitate in the filter, and heat gently in a covered platinum crucible until the paper is carbonized, and then ignite strongly over the blast. The heating should be continued until the silica is pure white, and the crucible should be covered when heating over the blast, or the strong current may sweep particles of silica out of the crucible.

The silica must in all cases be tested for impurities. This is done by heating it with hydrofluoric acid or ammonium fluoride.* If a residue is left, its weight should be subtracted from the weight of the silica found. Dissolve the residue in sulphuric acid and add it to the main solution.

Some silicates contain titanic acid. This will be separated with the silica, unless an excess of hydrochloric acid is added to the dry residue; otherwise the most of the titanic acid is dissolved. To determine the titanic acid, fuse the residue left by hydrofluoric acid, with potassium bisulphate, dissolve the fuse in water, filter, if necessary, and precipitate the titanic acid by long continued boiling†. Pass a current of carbon doxide through the liquid while boiling, and replace the water lost by evaporation. Wash the titanic acid with water, and ignite, after adding a little solid ammonium carbonate. If a portion of the titanic acid has been dissolved, it will pass into the ammonium hydroxide precipitate. Fuse the latter with potassium bisulphate, dissolve the fuse in cold water, filter, and pass hydrogen sulphide through the filtrate to reduce the iron. After complete reduction, precipitate the titanic acid as given above.

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* These should contain no non-volatile constituents.

† [Compare: Determination of Titanic Acid in Magnetite.]

NATROLITE.

Hydrated Silicate of Aluminum and Sodium; occasionally with small amounts of Iron and Calcium.

Digest the pulverized and dried mineral with hydrochloric acid, and proceed as given above.

Heat the filtrate from the silica to boiling, and precipitate the iron and aluminum with a slight excess of ammonium hydroxide, which should be free from ammonium carbonate. Heat the covered dish until the odor of ammonia can scarcely be detected. Filter, and wash the precipitate with hot water, ignite and weigh.

If the amount of calcium present is very large, the precipitate obtained above is not pure. After precipitating with ammonium hydroxide, at once acidify with acetic acid, and then nearly neutralize with ammonium hydroxide, leaving the solution with a slight acid reaction. Or, decant the clear supernatant liquid through a filter, dissolve the precipitate in hydrochloric acid, dilute, and reprecipitate.

The weighed alumina contains all the iron as ferric oxide, and also generally contains a small amount of silica. Dissolve the precipitate in strong hydrochloric acid, evaporate the excess, filter out the silica and determine the iron in the filtrate volumetrically.

Precipitate the calcium in the filtrate from the iron and aluminum with ammonium oxalate, and ignite the precipitate to calcium oxide. More or less alkali passes into the calcium oxalate; it is necessary, therefore, to dissolve the precipitate in hydrochloric acid after filtration, and reprecipitate with ammonium hydroxide and a few drops of ammonium oxalate.

The filtrate contains ammonium salts, together with the sodium in the form of sodium chloride. Evaporate to dryness in a platinum or porcelain dish, expel the ammonium salts by gentle ignition, and transfer the non-volatile residue to a weighed platinum crucible. Cover, ignite gently and weigh as sodium chloride.

Determination of Water:—Ignite a sample of the dry powder to constant weight in a platinum crucible. It is advisable to use coarse powder, or even small pieces, for this determination, as the draught of the flame may carry away small particles.

PREHNITE.

Hydrated Aluminum-Calcium Silicate, ordinarily with varying amounts of Iron, Manganese and Alkalies.

The analysis may be executed as given under Natrolite; in this case, however, a double precipitation of the calcium oxalate is necessary.

As prehnite generally contains but a small amount of maganous oxide (up to 0.3%) the latter may be precipitated as maganous sulphide in the filtrate from the calcium oxalate, by the addition of a few drops of ammonium sulphide. Determine as maganous sulphate, as given on page 39.

Acidify the filtrate from the maganous sulphide with hydrochloric acid, heat until the liquid no longer smells of hydrogen sulphide, and filter off the sulphur. Determine the alkalies, as usual, in the filtrate.

In determining the water, it should be noted that many varieties of prehnite, which contain organic substances, blacken on heating, owing to decomposition and carbonization of the organic matter, and become white only after heating for some time. In this case, the water must be determined by direct weighing. See pages 61 and 171.

If it is desired to determine the organic matter, one of the methods given below may be used. A weighed amount of the substance is heated with copper oxide in a current of oxygen, and the resulting carbon dioxide weighed. See : Organic Analysis.

DATOLITE.

Hydrated Calcium Silicate, with Calcium Borate, occasionally with Aluminum and Magnesium.

Treat the finely pulverized and dried mineral as given under Natrolite. After separating the silica, precipitate the iron and aluminum as hydroxides, with ammonium hydroxide free from carbonate. The precipitate always contains boric acid. To remove the latter, add hydrofluoric acid or ammonium fluoride to the precipitate in the crucible, mix, add a few drops of sulphuric acid and heat. This volatilizes the boric acid as boron fluoride. Add a little ammonium carbonate and continue the heating for some time, to expel the sulphuric acid.

Precipitate the calcium as calcium oxalate, and the magnesium as phosphate, as usual.

The boric acid is generally estimated by difference.

If it is desired to determine it directly, mix a weighed amount of the silica with 4 times its weight of potassium carbonate and fuse. Digest the fuse in hot water, filter, and wash the residue with hot water. Precipitate aluminum, calcium, and the most of the silicic acid, with ammonium carbonate, and the last traces of the silicic acid with a solution of zinc oxide in ammonium hydroxide. The solution is now free from silica, aluminum and calcium. Saturate with hydrofluoric acid and evaporate to dryness in a platinum dish.

Treat the residue with a 20% solution of potassium acetate. The potassium fluoborate is insoluble, and may be determined as such, as given on page 166.

Determine the water as given under Natrolite.

OLIVINE.

Silicate of Iron and Magnesium.

Digest the dried mineral with hydrochloric acid and separate the silica, as usual. The residue should not be heated to a temperature higher than that of the water-bath, otherwise basic salts of iron, which are difficulty soluble in hydrochloric acid, are formed. Oxidize the iron in the filtrate from the silica, boil, and precipitate with ammonium hydroxide.

Precipitate the magnesium, as usual, in the filtrate. If the olivine contains aluminum, the latter is contained in the precipitate with the iron. In this case, determine the iron volumetrically in a special sample.

Many olivines contain traces of copper, tin, manganese and nickel. Separate the first two with hydrogen sulphide in the filtrate from the silica. If the sulphide precipitate is not very small, digest with sodium sulphide, and filter. Determine the tin in the filtrate as given on page 84, and determine the insoluble cuprous sulphide, as such.

Add ammonium hydroxide and ammonium sulphide to the filtrate from the copper and tin, filter out the sulphides of nickel and manganese and treat them with a mixture of hydrochloric acid and hydrogen sulphide water. The nickel sulphide is insoluble ; ignite with access of air, and weigh at NiO. Precipitate the manganese in the filtrate, as manganous sulphide.

ILVAITE.

Silicate of Ferric and Ferrous Iron and Calcium ; ordinarily with small amounts of Aluminum and Manganese.

Decompose the mineral with hydrochloric acid and separate the silica, as usual. Heat the filtrate with hydrogen peroxide or nitric acid to oxidize the iron, neutralize the solution with sodium carbonate, and precipitate iron and aluminum with sodium acetate. See page 120.

The precipitate generally contains a small amount of silica. To separate the latter, digest the gently ignited and weighed precipitate with strong hydrochloric acid, evaporate the excess, dilute with water and filter. The alumina is calculated by difference, by deducting the silica found, and determining the iron in a separate sample. See below.

If the ferric oxide is not soluble in hydrochloric acid by reason of too strong ignition, it may be rendered soluble by fusion with potassium bisulphate.

Precipitate the calcium as oxalate in the filtrate from the ferric acetate, and then separate the manganese as sulphide, after neutralizing with ammonium hydroxide.

The ferric and ferrous iron may be determined as given under Magnetite, or the mineral may be dissolved in an atmosphere of carbon dioxide, then diluted to a definite volume without filtering out the silica, and the ferrous iron determined in one-half the solution and the total iron in the other half.

ULTRAMARINE.

Constituents: Aluminum, Sodium, Silica and Sulphur. As a rule, small amounts of Iron, Calcium, Potassium, Sulphuric Acid and Chlorine, are also present.

Digest the dry powder with hydrochloric acid ; hydrogen sulphide will be evolved, and silica (clay) and sulphur will be deposited. After complete decomposition, separate the silica, as usual. Ignite the silica and sulphur ; the sulphur will be burned, and the silica can be weighed as such.

The silica must be tested for impurities.

Precipitate the sulphuric acid in the filtrate, as usual, with barium chloride, and then remove the excess of the latter with dilute sulphuric acid.

Separate the alumina in the filtrate from the barium sulphate, by two precipitations, and test the precipitate for silica, after ignition. When alumina is precipitated in the presence of sulphuric acid, the latter always contaminates the precipitate. The aluminum hydroxide should therefore be strongly ignited. As strong ignition renders the alumina difficulty soluble in hydrochloric acid, it must be fused with potassium bisulphate, if it is desired to determine the iron. Dissolve the fuse in cold water and filter off the silica. A separate sample may also be used for the determination of iron.

Determine the calcium in the filtrate, as usual,

Determination of Alkalies :—Evaporate the filtrate to dryness, volatilize the ammonium salts by gentle ignition, and weigh the alkalies as sulphates.

Determination of Total Sulphur :—The sulphur can be oxidized to sulphuric acid, as given on page 147, or the sulphur may be oxidized by potassium chlorate and nitric acid, Sp. Gr. 1.36. Add 25 cc. of nitric acid to the substance in a covered dish, warm on the sand-bath, and then add potassium chlorate from time to time. When the oxidation is complete, cool, add hydrochloric acid and evaporate to dryness on the water-bath. Dissolve the residue in water, filter off the silica and precipitate the sulphuric acid with barium chloride.

If the solution contains undecomposed potassium chlorate or nitrate, the precipitate will be contaminated with barium chlorate or barium nitrate. The barium chlorate may be removed by digesting the ignited precipitate with dilute hydrochloric acid ; the barium nitrate, however, is only partly removed.

Care must therefore be taken that the nitrates are all decomposed, before precipitating with barium chloride. This may be done by evaporating to dryness several times on the water-bath, with hydrochloric acid.

In making the calculations, the amount of sulphuric acid present in the substance, as such, must be deducted from the amount found after oxidation of the sulphur.

The free sulphur may be determined by extracting a weighed amount of the ultramarine with pure carbon bisulphide; evaporate off the solvent and weighing the residual sulphur, after drying at 100° C.

If it is desired to determine the sulphur that is evolved as hydrogen sulphide on treating with hydrochloric acid, the apparatus shown in Fig. 34, or Fig. 21, may be used. The hydrogen sulphide is oxidized to sulphate.

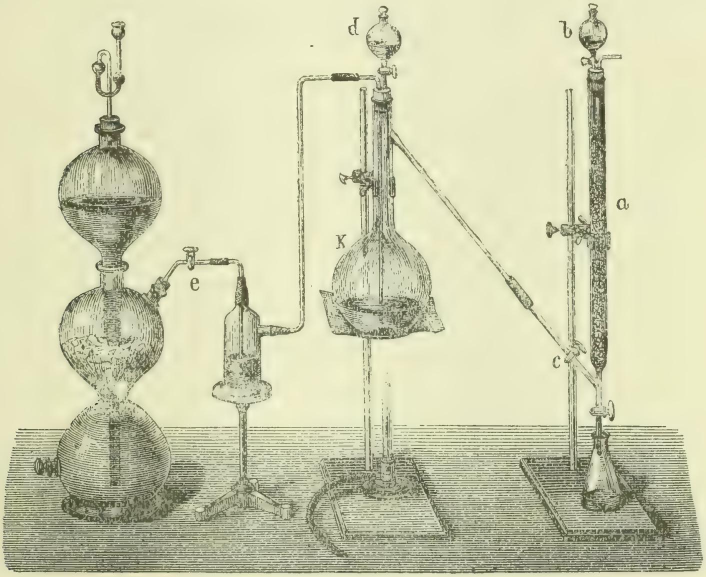

Fig. 34.

The decomposing flask K, of about 500 cc. capacity, is connected on one side with a hydrogen or carbon dioxide generator, and on the other side with an absorption tube a, filled with glass beads. The dropping funnel b, whose lower end is drawn to a small opening, is filled with an ammoniacal solution of hydrogen peroxide, or with a solution of bromine in 10% potassium bromide. The dropping funnel d, is filled with hydrochloric acid.

The other hole in the stopper (cork, not rubber) in the upper end of a, is provided with a tube which leads into a cylinder (not shown in the figure) filled with dilute sodium hydroxide. The latter serves to absorb liberated bromine vapors.

When the apparatus is ready, place the weighed substance in the flask K, and add enough water to immerse the lower end of the tube through which the gas enters. Now add the oxidizing solution from b, drop by drop, until the lower narrow part of the tube is full, and then gradually open the stop-cock of the funnel d. When no more gas is evolved on adding acid, gradually heat the contents of the flask to boiling, open the cock c and pass a slow current of gas until all the hydrogen sulphide is swept over and oxidized. If bromine solution is used for the oxiding agent, the solution is gradually decolorized; open the lower stop-cock and allow the solution to run out into a beaker, at the same time replacing it with fresh solution from b. Care must be taken that the beads are always moistened with fresh solution.

In no case should enough solution collect in a, to cause the liquid to back up into the wash bottle at e. No more liquid should be collected in a, than the pressure of the gas generator can overcome.

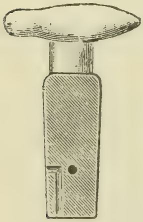

Fig. 35.

The stop-cock at c, should be a 3-way cock, Fig. 35, so that a small portion of the gas can be tested for hydrogen sulphide with lead acetate paper.

After complete decomposition, wash out the tube a, with water; if bromine was used, evaporate the excess and determine the sulphuric acid, as usual. The sulphuric acid can be determined much more conveniently if hydrogen peroxide is used, as the solution contains no substances which influence the precipitation. The precipitate is also more dense, settles quickly and is easily filtered.

The chlorine may be determined as usual.

REFINING SLAG.

Constituents: Ferric and Ferrous Iron, Metallic Iron, Manganese, Copper, Aluminum, Calcium, Magnesium, Silica, Sulphuric Acid, Phosphoric Acid and Titanic Acid.

Finely pulverize the slag and dry at 100° C. Decompose a weighed sample with hydrochloric acid, and separate the silica as usual. If the slag contains titanic acid, part of it will be with the silica.

The method of analysis is the same as was given under Iron Ores, to which reference should be made.

Ferrous iron is best determined in a special sample, by decomposition with concentrated sulphuric acid in a sealed tube*. If it is necessary to use hydrochloric acid in the decomposition, and the ferrous iron is to be titrated with permanganate, the precautions given on page 111, (note ‡), should be observed.

If the slag contains metallic iron, it may be determined by treating 5 grams in a platinum dish, with a solution of copper sulphate†. An amount of copper equivalent to the iron will be deposited.‡

After standing for some time, with occasioned stirring, filter out the copper and undecomposed slag, wash

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[*] [See: Hillebrand and Stokes, Relative value of the Mitscherlich and hydrofluoric acid methods for ferrous iron determinations. Jour. Am. Chem. Soc., Vol. 22, p. 625.]

[†] 10 grams of $CuSO_4+7H_2O$ in 1 liter of water.

[‡] $CuSO_4+Fe = FeSO_4+Cu$.

with water and digest with nitric acid to dissolve the copper. Expel the acid by evaporation and determine the copper as given on page 64.

If the slag itself contains copper, of course the corresponding amount should be subtracted.

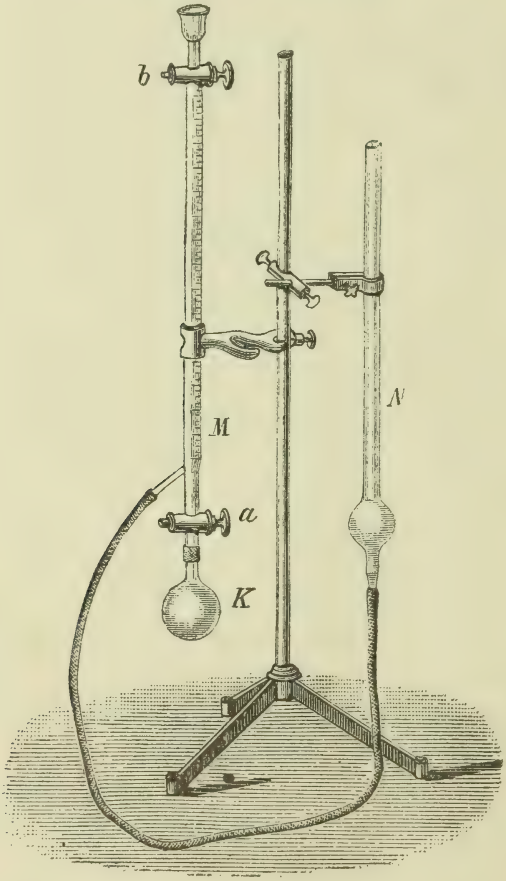

Fig. 33.

The preceding method gives reliable results only when the slag contains no substances which form insoluble compounds with the copper sulphate.

G. Neumann has based a method for the determination of metallic iron upon the determination of the volume of hydrogen evolved when the substance is treated with an acid:

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

The apparatus used is shown in Fig. 36.

Place the substance in the flask K, fill with water, and connect with the measuring tube M. Open the stop-cock a, raise the levelling tube N, and allow water to run into K until the opening in the stop-cock is filled. Now close the cock a, fill the levelling tube with acid, raise it and fill the tube M, and close the cock b. Open the cock a to allow the acid to diffuse downward; hydrogen is evolved. It is necessary to warm the flask K for some time, to completely decompose the slag. The hydrogen collects in M, and its volume is measured after the apparatus has assumed the temperature of the room, and the gas has been adjusted to atmospheric pressure with the levelling tube N.

See Determination of Nitrogen in Iron, for the reduction of the gas volume to 0° C. and 760 mm. pressure.

If the substance evolves hydrogen sulphide or carbon dioxide, after complete solution, lower N, and introduce potassium hydroxide colored with litmus tincture through the funnel above b; if the litmus turns red, more potassium hydroxide must be added. The two gases mentioned will be completely absorbed.

The ferrous iron formed when the metallic iron is dissolved in acids, must be subtracted from the ferrous iron found in the special sample.

The phosphoric acid and sulphuric acid may be determined as given on page 124.

COPPER AND LEAD SLAGS.

Constituents: Ferrous Iron, Aluminum, Manganese, Copper, Lead, Barium, Calcium, Magnesium, Alkalies, Silica, Sulphuric Acid and Sulphur*.

The bases may be determined as given under Psilomelane, page 135. Decompose the slag either with nitric acid, or with a solution of bromine in hydrochloric acid, and separate the silica as given on page 170.

If the slag contains a large quantity of lead, part of it may be separated with the silica in the form of crystalline lead chloride, and can be washed out only with difficulty. In this case, digest the silica repeatedly with hot water and decant onto the filter.

Barium, if present, will also be found with the silica, as barium sulphate. Warm the weighed precipitate with hydrofluoric acid, or mix with ammonium fluoride and volatilize the silica as silicon tetrafluoride; weigh the barium sulphate and calculate the silica by difference.

To determine the lead, add sulphuric acid and evaporate to expel the hydrochloric acid. Determine the lead sulphate as given on page 63.

In the presence of much iron, the lead sulphate may be contaminated with that element, if the evaporation is carried too far; it is preferable, therefore, to evaporate only the greater part of the hydrochloric acid. Now add ammonium hydroxide until a permanent precipitate is formed, and then dissolve the latter in sulphuric acid. Add one-third the volume of the solution of alcohol to decrease the solubility of the lead sulphate.

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* The slag may also contain; Arsenic, Antimony, Bismuth, Zinc, Cobalt, Nickel, etc. For the determination of these elements, see analysis of Refined Lead, and analysis of Black Copper.

Expel the alcohol from the filtrate, precipitate the copper with hydrogen sulphide and determine it as cuprous sulphide, as given on page 65. If antimony or arsenic are present, the sulphide precipitate must be digested with sodium sulphide; the arsenic and antimony sulphides dissolve and the copper sulphide remains insoluble.

Boil off the hydrogen sulphide, oxidize the iron, precipitate the latter as basic carbonate or acetate, and determine the manganese, calcium and magnesium in the filtrate, as usual.

It is best to determine the alkalies in a special portion. Separate the silica, pass hydrogen sulphide to precipitate the copper group, and add ammonium sulphide and ammonium oxalate to the filtrate. After complete precipitation, filter, and decompose the excess of ammonium sulphide with hydrochloric acid; boil off the hydrogen sulphide and filter out the sulphur. Evaporate the filtrate to dryness, expel the ammonium salts by gentle ignition and separate the magnesia from the alkalies, as given on page 105. Determine the alkalies as sulphates. See page 104 for the method of separation of the alkalies.

If the slag evolves hydrogen sulphide on being treated with dilute acid, it may be determined as given on page 181.

Determine the sulphuric acid in a special portion.

Determination of Silica in Silicates not Decomposable by Acids.

If a silicate is mixed with sodium or potassium carbonate and fused, a more basic silicate, which is decomposable by acids, is formed.

Finely pulverize the silicate, dry it at 100° C., mix with about 9–10 times its weight of a mixture of sodium and potassium carbonates (5 :7), by stirring with a platinum spatula or glass stirring rod, and fuse in a platinum crucible until no more carbon dioxide is evolved and the mass is in quiet fusion. If an ordinary Bunsen burner is used, about half an hour will be required for complete decomposition ; if a blast lamp is used, about 10 minutes will be sufficient. If a platinum dish is at hand, pour the contents of the crucible into it, or proceed as given on page 64. Add about 20–30 times the amount of water to the fuse in a beaker, and warm on the water-bath until all soluble matter is in solution.

Now add hydrochloric acid as long as effervescence is produced, rinse off the crucible, warm on the water-bath to decompose the last of the silicate and to expel the absorbed carbon dioxide. Evaporate the solution to dryness in a platinum or porcelain dish, to separate the silica held in solution*, and heat in an air-bath at 120° C. until the residue appears perfectly dry ; proceed as given on page 172. To be certain that all the salts pass into solution, it is advisable to treat the silica a few times with warm, dilute hydrochloric acid before transferring it to the filter.

Wash the silica with hot water until all the salts are washed out ; dry, ignite and weigh, as given on page 173.

Determination of Alkalies in Silicates not Decomposable by Acids.

If a silicate is decomposed by fusion with alkaline carbonates, the determination of alkalies is excluded, and other means of decomposition must be used if the alkalies are to be determined.

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* Under certain conditions, the silica may also remain entirely dissolved in the acid used, especially if a large excess of alkaline carbonate was used in the decomposition; this may also happen, if there is but a small amount of silica present.

Use either a mixture of hydrofluoric acid and sulphuric acid, pure hydrofluoric acid or ammonium fluoride*.

If a silicate is warmed with hydrofluoric acid or ammonium fluoride, volatile silicon tetrafluoride is formed; the metals remain in the residue as fluorides. On treating the metallic fluorides with concentrated sulphuric acid, they are decomposed and form soluble sulphates.

Decomposition with Hydrofluoric Acid:—Finely pulverize and dry the mineral, and treat it in a platinum dish with concentrated hydrofluoric acid, or better, with a mixture of 1 part sulphuric acid (1 part acid to 1 part water) and 2–3 parts of hydrofluoric acid, and heat nearly to boiling. When decomposition is complete†, evaporate to dryness, and heat until all the sulphuric acid is expelled; the temperature should not be raised too high, as the bases are rendered difficultly soluble.

After cooling, warm the residue with concentrated hydrochloric acid, add a little water and continue the heating for some time. If a part of the residue remains undissolved, it may be undecomposed mineral, or barium sulphate, if the mineral contains barium. The residue should then be tested qualitatively, and the treatment with hydrofluoric acid repeated, if necessary.

Decomposition with Ammonium Fluoride:—In decomposing a silicate, ammonium fluoride has the advantage over hydrofluoric acid that it is easily prepared in a pure state.

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* It should be noted that the decomposition of silicates by hydrofluoric acid or ammonium fluoride, is much facilitated by previous ignition.

† Most silicates are quickly decomposed; 10–15 minutes generally being sufficient time.

and also that some silicates, which are but slowly attacked by hydrofluoric acid, e. g., tourmaline, are easily decomposed by ignition with ammonium fluoride.

Mix the finely pulverized and dried silicate in a platinum crucible with 7–8 times its weight of ammonium fluoride, moisten the mass with a little water and warm on the water-bath until perfectly dry; then heat over a small flame until no more vapors are evolved. To decompose metallic fluorides and silico-fluorides, add a few drops of concentrated sulphuric acid, expel the excess by gentle ignition and then dissolve the residue in hydrochloric acid. If it is desired to form chlorides of the bases, the method described on page 139, foot note, may be used.

[Decomposition with Ammonium Chloride and Calcium Carbonate. Method of J. Lawrence Smith*:—Intimately mix 1 gram of finely ground silicate with an equal weight of granular ammonium chloride. Add 8 grams of calcium carbonate and grind the entire mass so as to obtain an intimate mixture. Transfer to a large crucible, cover with a close-fitting cover and heat carefully for a few minutes to decompose the ammonium chloride. Gradually heat to redness and maintain at this temperature for about an hour. Cool, place in a large platinum dish, fill the crucible with water and allow to digest over night. Rinse out the crucible, add about 100 cc. of water, and heat to complete disintegration. Filter into another platinum dish and wash with hot water; add about 1.5 grams of pure ammonium carbonate, evaporate on the water-bath until the volume of the solution is reduced to about 40 cc.; add a little more ammonium carbonate and a few drops of ammonium hydroxide and filter on a small filter. Evaporate the filtrate carefully, after adding a few drops of ammonium carbonate to be sure that all the calcium has been precipitated.

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* [Am. Jour. Sci. Vol. 50, p. 269.]

If any further precipitate appears, filter into a platinum crucible and evaporate to dryness. Heat carefully to dull redness to expel ammonium salts, cool and weigh as potassium-sodium chloride. Separate the alkalies as given on page 103.]

Decomposition of Silicates With Boric Oxide.

According to Jannasch, silicates may also be decomposed by fusion with boric oxide. The advantage of this method over the others is that it neither introduces foreign substances (alkalies) into the solution, nor eliminates one of the essential constituents of the silicate (silica), as after solution, the boric oxide is completely volatilized.

On fusion, the mass commonly froths, and it is advisable to effect the decomposition in a crucible of 50–60 cc. capacity. Place about 1–1.25 grams of the very finely pulverized silicate in the crucible and mix with from 3–8 times as much alkali-free boric oxide that has previously been fused and finely pulverized*. Feldspar requires about 8 times as much boric oxide for decomposition, as was taken of silicate for analysis.

The crucible should be heated at first over a small flame, until the moisture is expelled, and the temperature then increased until complete fusion is effected; allow to remain in quiet fusion for about 10 minutes, and then heat for about 15 minutes over the blast lamp†.

Dip the glowing hot crucible in cold water, after covering it to avoid loss by decrepitation. Transfer the fused mass to a porcelain dish, add about 200–250 cc. of boiling water and 50–75 cc. of hydrochloric acid; stir and heat until all is in solution except a few particles of silica. Dissolve the particles adhering to the crucible with hydrochloric acid, and add to the solution in the dish. Evaporate the solution on the water-bath, when the silica will separate in a gelatinous form; constant stirring is now necessary to bring the mass to dryness.

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* The pulverized boric oxide should leave no residue when heated with the methyl chloride described below.

† Jannasch is of the opinion that the decomposition is effected either by the boric oxide expelling the silica at the high temperature used, or by boro-silicates being formed, which are decomposable by hydrochloric acid.

To remove the boric oxide, heat the mass with methyl chloride which forms volatile boric ether. Heating with methyl alcohol and hydrochloric acid will not form the ether; it is therefore necessary to previously form the ester by saturating about 250 cc. of pure anhydrous methyl alcohol with dry hydrochloric acid gas; an ordinary alcohol washing bottle, with ground glass stopper, answers very well.

After being made for some time, the ester loses its effectiveness; it may be regenerated, however, by again saturating with hydrochloric acid gas.

Add about 60–75 cc. of methyl chloride to the dry residue, stir until all the soluble matter is in solution and heat on the water-bath to 75–80° C., while constantly stirring.

As soon as the alcohol is all expelled, repeat the operation, rinsing down the particles of boric acid that adhere to the sides of the dish. A third and fourth evaporation with methyl chloride is advisable to remove the last traces of boric oxide.

After heating the dry mass as given on page 172, treat the residue further, as there described.

It is recommended to evaporate the filtrate from the silica a second time, (for greater certainty, treat the residue again with methyl chloride) to separate the small amount that passed into solution during the first treatment.

After weighing the silica, never neglect to moisten it with 10–15 drops of dilute sulphuric acid and then to heat it with pure hydrofluoric acid; any residue remaining after this treatment cannot be silica, and should be subtracted from the original weight.

The decomposition with boric oxide can also be used for determining silica in quartz. The method is a generally applicable one.

Decomposition of Silicates by Hydrochloric Acid Under Pressure.

As the glass of the pressure-tube, as well as the mineral, is attacked by the acid, Jannasch places the substance in a platinum tube of the form shown in Fig. 37 (1/3 the natural size). The tube can be closed by a cap into which a platinum tube is soldered; on the side of the tube there is a small loop to which a platinum wire can be fastened and by means of which the tube can be introduced into, and removed from, the glass tube.

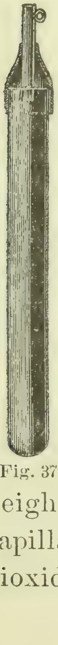

Fig. 37.

After placing the powdered silicate in the tube, add about 10 cc. of hydrochloric acid (4 Vol. acid to 1 Vol. water), mix with a platinum wire, close the tube with the cap and lower it by means of a platinum wire, into a strong-walled pressure tube of potash glass. Add sufficient hydrochloric acid to surround the platinum tube up to about half its height and then draw out the end of the tube to a strong capillary and seal it off, after replacing the air by carbon dioxide. In an atmosphere of carbon dioxide the platinum is attacked less than in an atmosphere of air; however, traces of platinum are always dissolved. Especial care should be taken that the acid used contains no free chlorine.

To effect complete decomposition, the tube should be heated at a temperature of 190–250° C. for 10–12 hours, in a bomb furnace. After cooling the tube, open it and empty the contents into a porcelain dish. Evaporate to dryness, stirring the contents of the dish towards the end of the evaporation; filter off the silica as given on page 170. A protracted heating in an air-bath, to render the silica insoluble, is not necessary in this method. On account of the exceedingly fine subdivision of the silica, a double filter should be used. Treat the filtrate with hydrogen sulphide, to precipitate the small amount of platinum dissolved.

FELDSPAR.

Potassium-Sodium-Aluminum Silicate, with Iron, Calcium and Magnesium.

Determination of Silica, Alumina, Ferric Oxide, Calcium and Magnesium :—Finely pulverize the mineral, dry it at 100° C. and fuse it with 4–5 times its weight of potassium-sodium carbonate and determine the silica exactly as given on page 188. The mineral may also be decomposed by boric oxide. See page 191.

Separate the alumina in the filtrate from the silica, by a double precipitation with ammonium hydroxide free from ammonium carbonate. See: Natrolite, page 174. If the feldspar contains iron, it may be determined volumetrically, after solution of the precipitate in hydrochloric acid or fusion with potassium bisulphate. If the iron is present in considerable quantity, it is better to determine it in a special sample of the substance.

The silica found on dissolving the ignited alumina precipitate in hydrochloric acid, must be subtracted from the weight of the alumina and added to the weight of the silica originally found.

Calcium and magnesium are separated, as usual, with ammonium oxalate and sodium-ammonium phosphate, respectively.

Determination of Alkalies :—Decompose the mineral with hydrofluoric acid or ammonium fluoride*, and proceed as given above. If the sample taken for the principal analysis was decomposed by boric oxide, the alkalies may be determined in the same sample. In the hydrochloric acid solution, precipitate the alumina with ammonium hydroxide and the calcium with ammonium oxalate. Precipitate the sulphuric acid in the filtrate from the calcium oxalate, with barium chloride, filter, and precipitate the excess of barium with ammonium carbonate ; separate the magnesia from the alkalies, as given on page 105. Determine the potassium as potassium-platinic chloride, as given on page 104 ; the sodium is obtained by difference.

CLAY.†

Hydrated Aluminum Silicate. Always contains more or less Ferric and Ferrous Iron, Manganese, Calcium and

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* [Or by the method of J. Lawrence Smith. See page 190.]

† For the mechanical analysis of Clay, refer to Fresenius: "Untersuchung der wichtigsten Nassauischen Thone" Jour. f. prakt. Chem., Vol. 57, p. 65.

Magnesium, Carbon Dioxide, Alkalies, Organic Matter, Quartz Sand and Titanic Acid.*

To determine the silica, mix the finely pulverized clay with 9–10 times its weight of potassium-sodium carbonate, and fuse. Dissolve the fused mass in hydrochloric acid, and separate and determine the silica†, alumina and iron as given on page 123. Dissolve the weighed alumina-iron precipitate in dilute sulphuric acid (8 parts acid : 3 parts water), filter out the silica, reduce the iron with zinc and titrate with permanganate. See Volumetric Analysis.

Precipitate the calcium as oxalate, in the filtrate from the alumina, etc., evaporate the filtrate to dryness and volatilize the ammonium salts by gentle ignition. Dissolve the residue in dilute hydrochloric acid and determine the magnesia as given on page 27. If the clay contains manganese, it will be found with the calcium; determine it iodometrically (page 149), or as sulphide (page 144), after solution of the precipitate. The manganese should be calculated to Mn_2O_3, and its weight subtracted from that of the calcium precipitate.

Determine the alkalies in a special sample, in case boric oxide was not used for the decomposition. Dissolve the fused mass in hydrochloric acid, precipitate the silica, alumina, iron, manganese, calcium and magnesium by the addition of ammonium hydroxide, ammonium oxalate and a little ammonium sulphide, and filter. Acidify with hydrochloric acid, to decompose the excess of ammonium sulphide, filter out the sulphur, evaporate to dryness and volatilize the ammonium salts. Separate the magnesia from the alkalies as given on page 105.

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* See page 123, for the determination of titanic acid, and the volumetric determination of iron in the presence of titanic acid.

† The silica must be tested for purity as given on page 173.

If the clay contains sand, besides chemically combined silicic acid, it may be determined as follows: Heat a weighed sample in a platinum crucible with an excess of concentrated sulphuric acid for 10–12 hours, allowing the acid to slowly evaporate. Dissolve the residue by warming with hydrochloric acid, filter out the silica and sand, and separate them as given on page 127.

If the clay contains pyrites, the sulphur may be determined by oxidizing a sample with concentrated nitric acid and potassium chlorate; expel the nitric acid by evaporation with hydrochloric acid, and precipitate the sulphuric acid by barium chloride.

The hygroscopic water can be determined by heating the air-dried clay for a long time in an air-bath at 120° C.

Presupposing the clay to contain neither organic matter nor ferrous iron, the water of constitution may be determined by igniting a weighed sample in a platinum crucible. Otherwise, the water must be determined directly as given on pages 61 and 170; in which case the 'loss on ignition' would give approximately, the amount of water and organic matter, as there is generally but little ferrous iron present.

If the clay contains carbonate, the 'loss on ignition' is not at all applicable, as carbon dioxide would be evolved.

In any case, it is best to determine these constituents directly, as given under the preceding examples.

GLASS*.

Constituents: Potassium, Sodium, Aluminum, Calcium, Magnesium, Silica, Sulphuric Acid, Phosphoric Acid, and Boric Acid.

In colored glasses, the metals giving the various colors, must be considered. If the glass contains only potassium, sodium, aluminum, iron, calcium, magnesium and silica, the method given under Feldspar may be used.

If the glass contains easily reducible metals, e. g. lead and tin, add a little potassium nitrate before fusion†.

If the glass contains lead silicate, the silica must be repeatedly washed with hot water to remove the lead chloride. Precipitate the lead as sulphide, in the filtrate from the silica, by passing hydrogen sulphide. Boil off the hydrogen sulphide, oxidize the iron with nitric acid and use the solution for the determination of the remaining metals.

Tin, if present in the glass, will be found in greater part with the silica; after weighing the silica, digest it with sodium sulphide or ammonium sulphide, filter, and determine the tin in the filtrate, as given on page 84. The filtrate from the silica should also be tested for tin, and if both tin and lead are present, separate their sulphides by digestion with ammonium sulphide; the insoluble lead sulphide may be determined as such, and the tin may be determined in the filtrate as given on page 84, after acidifying with dilute sulphuric or hydrochloric acid.

In the presence of manganese, the alumina should be precipitated with sodium acetate, after neutralization with sodium carbonate, instead of precipitating it with ammonium hydroxide; precipitate the manganese in the filtrate from the alumina, with ammonium sulphide.

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* Porcelain and Kaolin may also be analyzed by the same method. See also: Analysis of Clay.

† [When fusing substances containing an easily reducible metal, care must be exercised or the platinum will be alloyed, and the vessel ruined.]

Cobalt, if present, will be precipitated with the manganese. Dissolve the sulphides in hydrochloric acid, with the addition of a little nitric acid, concentrate, and separate the cobalt as potassium-cobalt nitrite as given on page 34; precipitate the manganese in the filtrate as sulphide. Manganese and nickel may also be separated by nitroso-β-naphthol.

If the glass contains zinc, the alumina should be separated as basic acetate, and the zinc precipitated in the filtrate by hydrogen sulphide.

Sulphuric acid may be precipitated with barium chloride in the filtrate from the silica, and the excess of barium removed, with dilute sulphuric acid, after filtering out the barium sulphate.

In the analysis of a glass which contains phosphoric acid, e. g. alabaster glass, after separating the silica, precipitate the phosphoric acid with metallic tin as given on page 149, and use the filtrate for the determination of the other elements.

See page 165 for the determination of Boric Acid.

EPIDOTE.

Silicate of Aluminum, Iron and Calcium, together with Ferrous Iron, Manganese, Magnesium, Potassium, Sodium and Water.

To determine the silica and the metals with the exception of the alkalies, fuse the pulverized, dry mineral, with potassium-sodium carbonate, and separate the silica as given on page 187. Heat the filtrate with hydrogen peroxide or nitric acid, and separate the iron and alumina from manganese and the alkaline earths, by sodium acetate, after neutralization with sodium carbonate.

Filter out the basic acetates of iron and alumina, and precipitate the manganese as sulphide, and the calcium and magnesium, as usual.

Ferric and ferrous iron may be determined quite accurately by decomposing the finely-ground mineral with sulphuric acid in a sealed tube, and then titrating with permanganate. Subtract the total iron, calculated to ferric oxide, from the weight of the alumina.

Cooke decomposed the mineral in an atmosphere of carbon dioxide and steam, to protect the ferrous iron from oxidation. A water-bath, Figs. 38 and 39, with a constant-level attachment, may be used, by soldering the tube a on the upper part; carbon dioxide, generated from a Kipp's apparatus, is passed into the apparatus through the tube a.

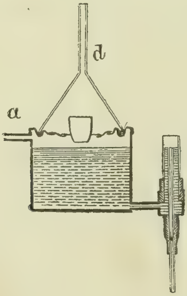

Fig. 38.

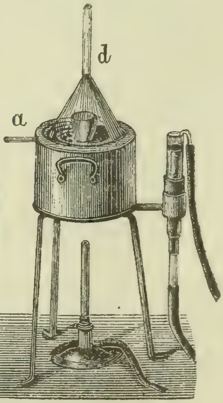

Fig. 39.

The cover of the water-bath is provided with a depression in which to set the funnel d. The ring carrying the platinum crucible should have a number of holes punched in it, to allow the steam to rise in the funnel ; the steam condenses on the sides of the funnel, runs down into the depression and forms a seal against the entrance of air.

Determine by a preliminary experiment, the minimum amount of hydrofluoric acid that must be added to sulphuric acid of Sp. Gr. 1.5, to decompose the mineral. Place about .5 grams of the finely pulverized mineral in a platinum crucible, add the necessary amount of sulphuric acid and hydrofluoric acid* and stir with a platinum spatula. Now place the crucible on the water-bath, cover with the funnel and fill the depression with water, replace the air in the apparatus by carbon dioxide, heat the water in the bath to boiling and continue the passage of the carbon dioxide until the funnel is filled with steam. After complete decomposition, remove the flame from beneath the bath, again pass carbon dioxide, and allow a current of cold water to run through the water-bath to hasten the cooling.

During the decomposition, the contents of the crucible may cake together and prevent further action of the acid ; in that case, remove the burner, fill the funnel with carbon dioxide and stir the contents of the crucible with a strong platinum wire introduced through the stem of the funnel. Rinse off the platinum wire and continue the heating, at the same time checking the current of carbon dioxide.

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* Commercial hydrofluoric acid should not be used direct, as it generally contains organic substances which are oxidizable by permanganate. The acid must first be distilled from a platinum retort, after addition of permanganate.

Determine the alkalies as given under Feldspar. The most accurate method for determining the water is by direct weighing. See pages 76 and 170.

BLAST FURNACE, CUPOLA, AND BESSEMER SLAGS.

Constituents: Ferrous and Ferric Iron, (under certain conditions, Metallic Iron), Manganese, Aluminum, Copper, Lead, Zinc, (Barium), Calcium and Magnesium, (Alkalies), Silica, Titanic Acid, Sulphuric Acid, Phosphoric Acid, and Sulphur (as Calcium Sulphide).

If the slag is decomposable by concentrated hydrochloric acid, digest a sample with a solution of bromine in hydrochloric acid and evaporate to dryness. Moisten the dry residue with hydrochloric acid, add water and warm; filter off the silica and again evaporate to dryness.

If the slag contains titanic acid, it is necessary to repeatedly wash the silica with warm, dilute hydrochloric acid. If the slag contains barium, it will be found with the silica in the form of sulphate; determine the weight of silica + barium sulphate, fuse the mixture with sodium carbonate, and proceed as given in the determination of barium in Barite.

Determine the remaining bases as given in the preceding examples.

If the slag is not decomposable by hydrochloric acid, proceed as given in the analysis of Epidote. Fuse the slag with potassium-sodium carbonate and first remove the alkaline salts by extraction with water. After separating the silica, the filtrate may be used for the determination of sulphuric acid, as given on page 124.

The phosphoric acid is determined in a special sample. See: Hematite.

The following method may also be used to determine the metals in the slag. Fuse the finely pulverized slag with potassium-sodium carbonate, and separate the silica* as given under Natrolite. In the presence of titanic acid, use an excess of hydrochloric acid to dissolve the residue, and determine the titanic acid as given on page 124.

If the slag contains lead or copper, precipitate them in the filtrate from the silica, after reducing the iron with sulphuric dioxide, by passing hydrogen sulphide. If both metals are present, dissolve the sulphide precipitate in nitric acid and separate the lead from the copper with sulphuric acid; if but one of the two metals is present, the sulphide precipitate may be ignited in a current of hydrogen and weighed as such.

Boil off the hydrogen sulphide, oxidize the iron with hydrogen peroxide or nitric acid, and precipitate the iron and alumina with sodium acetate. The precipitate should be tested for silica and titanic acid†. See page 173.

Add acetic acid to the filtrate, and precipitate the zinc by hydrogen sulphide; the manganese may be precipitated in the filtrate from the zinc, by the addition of ammonium sulphide.

Filter out the manganous sulphide, and determine the calcium and magnesium, as usual.

Determine the ferrous iron according to the method given under Epidote, or Magnetite.

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* See page 186, for the determination of barium sulphate in the presence of silica.

† For the determination of barium sulphate in silica, see above.

The method for determining metallic iron is given on page 185.

To determine the alkalies, decompose a special sample according to one of the methods given on page 188, and proceed, in general, as given under Copper and Lead Slags.

If the slag contains calcium sulphide, determine the sulphur by oxidizing the liberated hydrogen sulphide with hydrogen peroxide or bromine solution. See pages 80 and 180.

Determine sulphuric acid and phosphoric acid as given under Hematite.

TOURMALINE.*

Constituents: Ferric and Ferrous Iron, Manganese, Aluminum, Calcium, Magnesium, Potassium, Sodium, Lithium, Silica, Boric Acid, Fluorine, Phosphoric Acid and Water.

Determination of Silica and Boric Acid:—Pulverize and dry the mineral, and fuse a sample with 4 times its weight of potassium carbonate; dissolve the fuse in water, filter out the insoluble matter and wash it thoroughly with hot water. The filtrate contains all of the boric acid together with a part of the alumina and silica; the latter are precipitated with ammonium carbonate or ammoniacal zinc oxide, as given under Datolite. After the filtrate has been entirely freed from silica and alumina, it may be used for the determination of boric acid. See: Ulexite, page 164.

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* [Compare: Riggs, Bull. 55, U. S. Geol. Surv., p. 19, and S. L. Penfield and H. W. Foote, Am. Jour. Sci., 1899, Vol. 7, pp. 97-125.]

Unite the original insoluble matter and the precipitate produced by ammonium carbonate and zinc oxide, add hydrochloric acid, and determine the silica as given under Natrolite, page 174.

Determine the iron, aluminum, manganese, calcium, magnesium and phosphoric acid, in a special sample. Decompose it by fusion with potassium-sodium carbonate, and proceed as given under Epidote.

Determination of Potassium, Sodium and Lithium:—Ignite a sample of the mineral at a full red heat for about an hour, decompose with hydrofluoric acid or ammonium fluoride, and follow the method given under Psilomelane, page 135.

Fluorine is generally calculated by difference; a direct method is given on page 150. The final precipitate obtained by calcium chloride, consists of calcium fluoride and calcium carbonate; calcium borate will also be precipitated if the mineral contains boric acid. The latter, together with the calcium carbonate, is dissolved when the precipitate is treated with acetic acid.

Determine the water as given on page 170.

CHROMITE.

Constituents: Chromic Acid, Ferrous and Ferric Iron, Alumina and Magnesia; occasionally with Manganese and Silica as impurities.

A number of methods for decomposing chromite have been recommended, of which the following have been found to be the most effective.

It is to be noted that the various varieties of the ore behave differently towards fluxes, and any one method cannot be recommended as the best, without preliminary experiments.

Mix the very finely pulverized ore with 3 times its weight of soda-lime, add 1/4 its weight of sodium nitrate and ignite for about 2 hours in a platinum crucible (Calvert).

Or, mix about .5 gram of the ore with about 4 grams of a mixture of 1 part potassium chlorate and 3 parts soda-lime, and ignite at a red heat for about 2 hours (Britton). According to Dittmar, the ore may be decomposed by fusing .5 gram with 5–6 grams of a mixture of 2 parts of borax glass and 3 parts of potassium-sodium carbonate; the mixture should previously be fused to expel the carbon dioxide.

[A very effective method for decomposing chromite is by fusion with 4–5 parts of pure sodium peroxide. The ore is completely decomposed in 15–20 minutes, and furthermore does not require extra fine pulverization. Thoroughly mix the ore and sodium peroxide with a platinum spatula, and heat at first with a very small flame; the mixture fuses at a very low temperature and tends to spatter, if heated too strongly.*

A copper or nickel crucible should be used for the decomposition and under no circumstances should a platinum vessel be used, as it will be ruined.]

The preceding methods are especially recommended when chromium and iron alone are to be determined. Extract the fused mass with water, and filter; the filtrate contains all the chromic acid. The iron can be determined in the residue.

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* [McKenna, Eng. and Min. Jour., 1898, p. 607.]

For a complete analysis of the mineral, fuse about .5 gram of the ore with about 4 grams of pure, previously ignited sodium carbonate, for about 2 hours in a covered platinum crucible at a low red heat*.

In the determination of chromium alone, if the decomposition was effected by soda-lime, the solution will contain silica, alumina and calcium as well as the chromate. Acidify with hydrochloric acid, pass hydrogen sulphide, filter, and evaporate the filtrate to dryness on the water-bath; dehydrate at 110° C., as usual.

After cooling, warm the residue with dilute hydrochloric acid, dilute with water, filter out the silica and wash it with hot water. To separate the chromium from the aluminum, the former must be oxidized to chromic acid. For this purposs, neutralize the solution with sodium carbonate, add sodium acetate in excess, and either pass chlorine gas, or add bromine water until the solution is colored.

Now precipitate the alumina with ammonium hydroxide, filter, reduce the chromic acid and precipitate it as hydroxide.

As seen above, the gravimetric determination of chromium is very tedious. In practice, therefore, the chromium is generally determined volumetrically. For this purpose, dissolve the fused mass in water, acidify with sulphuric acid and add a weighed excess of ferrous-ammonium sulphate, $FeSO_4.(NH_4)_2 SO_4+6H_2O$; titrate the unoxidized ferrous iron with permanganate. 6 equivalents of ferrous iron require 2 equivalents of chromic acid for oxidation to ferric iron. See: Siderite, page 113.

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* It should not be forgotten that the crucible will be attacked, and that sometimes considerable platinum will pass into solution.

The chromium may be titrated in a similar manner, if either of the other methods have been used for the decomposition.

Gravimetric Determination of Chromium :—Digest the fuse with water, filter, acidify the solution and precipitate the platinum by passing hydrogen sulphide. Separate the silica by evaporation, filter, and determine the chromium as chromic oxide, Cr_2O_3, according to one of the methods given on page 43.

The portion of the fuse insoluble in water, contains the iron, aluminum, manganese, calcium and magnesium. Proceed as given under Siderite.

According to Jannasch, the ore may also be decomposed by heating for 8–10 hours at a temperature of 270–290° C. in a sealed tube with a mixture of 4 parts of hydrochloric acid and 1 part water. If chromium only is to be determined, the sample and acid may be placed directly in the tube ; if, however, a complete analysis is to be made, the mineral should be placed in the platinum tube described under Decomposition of Silicates, as the glass is attacked by the acid at a high temperature.

Empty the contents of the tube into a porcelain dish, evaporate to dryness, dissolve in hydrochloric acid and water, and filter out the silica. Pass hydrogen sulphide through the filtrate to precipitate the platinum. The solution of the platinum can be largely prevented by filling the tube with carbon dioxide.

Proceed as given on page 207.

To make a direct determination of the ferrous iron contained in chromite, place about .5 gram of the finely pulverized ore in a pressure tube, add 10 cc. of sulphuric acid, Sp. Gr. 1.34, displace the air by carbon dioxide, seal the tube and heat it in a paraffin-bath for about 10 hours at a temperature of 250–300° C. When the mineral is decomposed, break off the tip of the tube, rinse out the contents, and determine the ferrous iron by titration with permanganate*.

ZIRCON.

Zirconium, Iron, Calcium and Silica.

The mineral is difficultly decomposable by acids, or by fusion with sodium carbonate; the decomposition, however, can be effected very easily by fusion with potassium acid fluoride. After the decomposition, add concentrated sulphuric acid, evaporate the excess of the acid, and precipitate the zirconia with ammonium hydroxide. Wash the precipitate with hot water, ignite and weigh as ZrO_2. Observe the precautions given under Determination of Alumina, page 108.

If the zircon contains iron, it will be found in the precipitate of zirconia; in this case, add to the solution a quantity of tartaric acid sufficient to prevent the precipitation of either iron or zirconia by ammonium hydroxide. Now precipitate the iron with ammonium sulphide. Filter, wash, ignite to Fe_2O_3 and weigh.

Evaporate the filtrate to dryness in a platinum dish, and ignite the residue to destroy the tartaric acid. The combustion of the carbon can be very materially hastened by moistening the residue with a saturated solution of ammonium nitrate, and repeating the ignition; if necessary, repeat the ignition with ammonium nitrate.

If no bases (calcium, etc.,) other than those introduced during the decomposition, are present, the residue obtained above may be repeatedly digested with boiling water, and the insoluble portion determined as ZrO_2. Otherwise, heat the residue with ammonium fluoride, dissolve in hydrochloric acid and precipitate with ammonium hydroxide. Filter off the zirconium hydroxide and determine the calcium in the filtrate, as usual.

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* [See Foot Note, p. 183.]

To determine the silica, a separate portion must be decomposed by fusion with sodium-potassium carbonate. Dissolve the fuse in hydrochloric acid and separate the silica as given on page 188.

Linnemann, in the analysis of zircon, used gaseous hydrofluoric acid to remove the admixed silicates; the solution is effected by allowing the acid to act for about a day. Linnemann decomposed the insoluble residue of zircon, by fusing it with 4 parts of a mixture of 10 parts sodium hydroxide and 1 part sodium fluoride.

PYRITE.

Constituents: Sulphur and Iron; ordinarily contains Arsenic, Antimony, Copper, Lead, (Gold), Zinc, Nickel, Cobalt, Manganese, Barium, Magnesium and Quartz, (Selenium).

In most cases, the sulphur contained in compounds decomposable by aqua regia is the only constituent determined in pyrites, as the other compounds of sulphur are not available for the manufacture of sulphuric acid.

Lunge has recommended the following method: The moisture is determined by drying a sample of the coarsely pulverized mineral at 105° C. to constant weight. Oxidize .5 gram with 10 cc. of a mixture consisting of 3 vols.

of nitric acid, Sp. Gr. 1.4, and 1 vol. of strong hydrochloric acid. Moisten the residue with hydrochloric acid, add about 100 cc. of hot water, filter, and wash with hot water. The insoluble residue may contain silica and silicates, together with sulphates of lead, barium and calcium ; ignite and weigh as insoluble matter.

Boil the filtrate, precipitate with ammonium hydroxide, and add barium chloride to the solution containing the precipitate of iron* ; acidify with hydrochloric acid, and proceed as given on page 24. Determine the barium sulphate as given on page 25.

To determine the total sulphur in pyrites, mix the finely pulverized substance in a platinum crucible, with about 10 times its weight of a mixture of 4 parts sodium carbonate and 1 part potassium chlorate, and fuse, beginning with a gentle heat. After cooling, transfer with hot water to a beaker, filter off the insoluble matter and wash it with hot water. Acidify the filtrate with hydrochloric acid and evaporate to dryness to separate the silica. Precipitate the sulphuric acid in the filtrate, as usual.

Determination of Copper, Lead, Arsenic and Antimony :—The simplest method for determining these constituents is the modified Fisher's Method, given on page 91. First eliminate the arsenic, and then precipitate the lead, arsenic and antimony remaining in the distilling flask, with hydrogen sulphide. Digest the sulphide precipitate with sodium sulphide, to separate the antimony sulphide. Determine the antimony according to the method given on page 79. The separation of copper from lead has been given above, page 65.

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* Kuester and Thiel. Zeit. Anorgan. Chem., Vol. 19, p. 97.

Determine iron, manganese, cobalt, nickel, calcium and magnesium, in a special sample. First precipitate the hydrogen sulphide group. (Lead, copper, antimony, arsenic). Add ammonium hydroxide and ammonium sulphide to the filtrate. Treat the precipitate with a mixture of hydrochloric acid and hydrogen sulphide water (page 136), filter off the insoluble sulphides of cobalt and nickel and separate them as given on page 33. Iron and manganese, as well as calcium and magnesium, may be determined as usual.

Determination of Gold :—If the mineral is fused with the sodium carbonate potassium chlorate mixture mentioned above, and the cooled mass is extracted with water, the gold will be found in the insoluble residue. However, as the amount of gold is extremely small, a larger quantity of substance must be taken and the decomposition effected in a Hessian crucible.

Ignite the insoluble residue consisting principally of ferric oxide, in a current of hydrogen, and dissolve the reduced iron (nickel, cobalt, etc.) in dilute nitric acid. If a portion is insoluble in nitric acid, dissolve it in aqua regia, filter out the silica and evaporate the filtrate to dryness on the water-bath.

Dissolve the residue in water, add it to the principal solution, acidify with a few drops of dilute sulphuric acid, and filter. Add an excess of concentrated ferrous sulphate or oxalic acid solution, and warm for some time. Filter out the precipitated metallic gold, wash, ignite and weigh.

If the pyrite contain selenium, as is commonly the case with Spanish ore*, fuse the finely-pulverized substance with a mixture of 2 parts sodium carbonate and 1 part potassium nitrate, extract with water and reduce the selenic acid to selenous acid by warming with hydrochloric acid; the selenium can now be precipitated in the elemental form with sulphur dioxide. See: Uraninite.

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* In the manufacture of sulphuric acid, the selenium passes, in part at least, into the acid. In the manufacture of sodium sulphate, it passes into the hydrochloric acid, and is generally detected by the red color imparted to the acid. After standing for some time, it settles out in the form of a red deposit.

The substance may also be fused with potassium cyanide in a current of hydrogen; the selenium then forms potassium-selenium cyanide, soluble in water. Dissolve in water, and precipitate the selenium in the elemental form by supersaturation with hydrochloric acid. A small amount will require several days for complete precipitation. As a portion of the selenium may form selenide, and be volatilized as hydrogen selenide on acidifying with hydrochloric acid, the water solution of the fused mass should be boiled for some time to form selenium cyanide.

Another method consists in heating the finely pulverized mineral in a current of oxygen in a combustion tube, and conducting the products of combustion into an absorption vessel containing water, in which the selenium is precipitated.

ROASTED PYRITES.

The slight amount of Lead, Copper, Zinc, Manganese, Aluminum, Calcium and Magnesium, may be determined by Rothe's method, given under Pig Iron; the Ferric Chloride is extracted by ether, while the remaining metals remain as chlorides, when the solution is evaporated.

Dissolve 10 grams of the pyrites in hydrochloric acid, with the addition of a little potassium chlorate. Evaporate the solution to dryness and dehydrate at 120° C.; dissolve the residue in 25 cc. of hydrochloric acid and 60 cc. of water. If the separated silica is not pure white, fuse it with potassium-sodium carbonate, and separate the pure silica as given on page 187. Boil the filtrate, acidify with hydrochloric acid, and precipitate the slight amount of iron, aluminum and lead with ammonium hydroxide ; dissolve the precipitate in hydrochloric acid and add to the main solution. The filtrate from the silica should also be tested with sodium sulphide, for traces of copper, zinc and manganese ; if any of these elements be found, dissolve the precipitate in hydrochloric acid and add to the main solution.

The precipitation is necessary, as the alkaline salts are precipitated in etherial solution, and clog the apparatus.

Concentrate the solution in a porcelain dish, until fumes of hydrochloric acid are driven off. Treat the contents of the dish as given under the ether extraction of iron in analysis of Pig Iron. If a small amount of lead chloride separates out, it does not interfere with the operation as it can easily be brought into solution again.

After freeing the solution from iron, precipitate the copper, lead and antimony with hydrogen sulphide, and separate the antimony sulphide from the remaining sulphides, by extraction with sodium sulphide, as usual.

Separate the aluminum and the trace of iron still in solution, from the zinc and manganese, by the acetate method. The separation and determination of the individual metals, as well as the determination of the calcium and magnesium, may be made as usual.

Arsenic, if present, will be partly or completely volatilized on heating the hydrochloric acid solution, and must be determined in a separate portion. The same is true of antimony in a less degree, and if extreme accuracy is desired, a separate portion of the substance must be used for their determination.

ARSENOPYRITE.

MISPICKEL.

Iron, Arsenic, (Antimony), and Sulphur.

The method may be inferred from the preceding examples. To determine arsenic, antimony and other metals of the hydrogen sulphide group, evaporate on the water-bath and remove the nitric acid by repeated evaporation with sulphuric acid. Separate the arsenic from the other metals by the method given on page 94, and precipitate the antimony in the liquid remaining in the distilling flask, by passing hydrogen sulphide. If lead and copper are present, proceed as given in the analysis of Pyrite.

Determine the iron and the remaining metals of the ammonium sulphide group, in the filtrate from the hydrogen sulphide precipitate.

CHALCOPYRITE.

Constituents: Copper, Iron, (Arsenic, Antimony), Sulphur, and Quartz.

The analysis, in general, is the same as given under Pyrite. In the absence of arsenic and antimony all the constituents can be determined in the same solution.

Dissolve the mineral in aqua regia, adding hydrochloric acid from time to time. Filter out the quartz, wash, ignite and weigh it as insoluble matter. Precipitate the sulphuric acid with barium chloride, remove the excess of the latter with dilute sulphuric acid, and precipitate the copper with hydrogen sulphide. Boil off the excess of the latter, oxidize the iron with hydrogen peroxide or nitric acid, and precipitate the iron with ammonium hydroxide.

If the mineral contains arsenic, it is best to follow the method given under Pyrite.

If antimony, as well as arsenic, is present in considerable quantity, mix the finely pulverized mineral with about 4 times its weight of ammonium chloride and gently heat in a covered crucible; this volatilizes almost all of the arsenic and antimony and the greater part of the iron, in the form of chlorides.* Digest the residue with nitric acid, and proceed as given above.

Many methods have been recommended for the volumetric determination of copper; the two that have acquired the most extended use, will be given.

Determination of Copper with Sodium Thiosulphate: —If potassium iodide is added to the solution of a cupr~~ous~~ salt, cuprous iodide will be precipitated, and an equivalent amount of iodine will be liberated. The free iodine can be determined with thiosulphate. See: Volumetric Analysis, Sodium Thiosulphate and Iodine.

To determine the copper by this method, dissolve the cuprous sulphide in nitric acid and evaporate to dryness. Dissolve the salt in water, add an excess of potassium iodide and titrate with sodium thiosulphate, using starch solution as an indicator.

If extreme accuracy is not required, dissolve the ore in aqua regia, evaporate down to nitrates, dissolve in water, precipitate with ammonium hydroxide, filter, and wash the precipitate and insoluble matter. Acidify the filtrate with hydrochloric acid and treat the solution as given above.

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* Classen, Zeit. f. anal, Chem., Vol. 18, p. 388.

The iron precipitate invariably retains copper; to recover this, dissolve the soluble portion of the precipitate in hydrochloric acid, and repeat the precipitation.

Determination of Copper with Potassium Cyanide:—When a solution of a cupric salt, e. g., $Cu(NO_3)_2$, is saturated with ammonium hydroxide, a deep blue solution results, containing $Cu(NO_3)_2.\,4NH_3$* If a solution of potassium cyanide is now added, the blue color disappears, owing to the formation of the colorless double cyanide:

$$2[Cu(NO_3)_2.4NH_3]+5KCN+H_2O=Cu_2(CN)_2.2KCN$$
$$+KOCN+2KNO_3+2NH_4NO_3+6NH_3.$$

The end reaction is the disappearance of the blue color.

The potassium cyanide solution should be standardized against an ammoniacal solution of a known amount of copper; this may be obtained by dissolving 10 grams of copper in nitric acid, saturating with ammonium hydroxide and diluting to 1 liter.

This method gives accurate results only when the same conditions are observed in standardizing the solution and in the actual analysis. The method is recommended for the determination of copper in low grade ores.

Steinbeck has recommended the following method:—Dissolve 4 grams of the finely pulverized, low-grade ore in 40–50 cc. of commercial hydrochloric acid, Sp. Gr. 1.16, and 6 cc. of dilute nitric acid, Sp. Gr. 1.10, by gently warming at first for 1/2 hour and then boiling for 10–15 minutes. This dissolves all the copper, as well as lead, zinc, iron, manganese and cobalt. Filter, and precipitate the copper in the filtrate with metallic zinc, or preferably, with cadmium. Test a drop of the solution with ammonium hydroxide to ascertain when reduction is complete.

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* [The blue solution probably contains this compound in a hydrated condition.]

Pour off the supernatant solution, wash the copper with water by decantation, and dissolve it in 8 cc. of 1.20 nitric acid. Cool the solution, add 10 cc. of ammonium hydroxide (1 vol. ammonium hydroxide Sp. Gr. .93, and 2 vols. water) and then titrate with potassium cyanide.

The potassium cyanide solution should be standardized against a copper solution of the same concentration, and containing the same amount of ammonium nitrate. The reagent should be added in the same manner, and at the same rate, in both cases.

Mohr advises to dissolve the ore in nitric acid and sulphuric acid, or hydrochloric acid and excess of sulphuric acid, and to evaporate to dryness. The filtrate is then free from hydrochloric acid, nitric acid and lead; pure lead-free copper can now be obtained by reduction with zinc. It is then simpler to weigh the copper directly, than to dissolve again and determine volumetrically.

[Electrolytic Determination of Copper:—Weigh out enough of the mineral to give a deposit of 100–150 milligrams of copper. Dissolve in a small casserole, in 20 cc. of conc. nitric acid, 5 cc. of conc. hydrochloric acid, and 5 cc. of conc. sulphuric acid, and heat on a hot plate until all the copper is dissolved, and fumes of sulphuric anhydride are evolved. Cool, add 50 cc. of distilled water, heat until all the copper sulphate is dissolved and then filter out the silica, etc., receiving the filtrate in a No. 1 beaker. Wash the residue with hot water, until free from copper. Nearly neutralize the excess of sulphuric acid with ammonium hydroxide, then add 2–3 cc. of conc. nitric acid.

It is best to deposit the copper on a cylindrical electrode having an area of at least 10 sq. in. Clean the cathode by washing in potassium hydroxide, dilute nitric acid and then with alcohol; heat the electrode to redness, cool in the dessicator, and weigh. The anode may be a smaller cylinder, or a spiral of stout platinum wire. Connect the cathode with the negative pole of the source of current and the anode with the positive pole. The two electrodes must not be in contact, and they should reach nearly to the bottom of the beaker. The current must have a voltage of at least 1.24 volts, to decompose copper sulphate, and from 0.1–0.25 amp. will give an adherent coating. Continue the passage of the current until the solution gives no test for copper with hydrogen sulphide water, on a white tile. When the copper is all deposited, siphon off the solution. replacing with distilled water, until the electrodes are sufficiently washed. Disconnect the cathode, rinse with alcohol, dry at a gentle heat so that the copper will not oxidize, cool in the dessicator and weigh. The increase in weight is copper.]

NICKEL OR COPPER MATTE.

Nickel, Cobalt, Zinc, Iron, Copper, Lead, Arsenic Antimony, Sulphur and Gangue.

It is most convenient to determine the constituents in two separate portions. Dissolve the finely powdered substance in aqua regia, by digesting on the water-bath.

To determine the arsenic, antimony, lead and copper, or to separate the arsenic from the remaining metals, the aqua regia must be evaporated, and the evaporation repeated, after addition of sulphuric acid. See page 215. The arsenic can now be volatilized in the form of chloride, as given on page 90, and the antimony, lead and copper, precipitated as sulphides, from the solution left in the distilling flask. The separation of these metals has been described above.

Before determining the other metals in the second portion, the metals of the hydrogen sulphide group must be removed*. In this connection, it should be remembered that arsenic pentasulphide is precipitated very slowly, and that the gas must be passed for some time, first warming the solution, and then allowing it to become cold.

Filter out the sulphide precipitate, boil off the hydrogen sulphide from the filtrate and oxidize the iron; precipitate the latter with ammonium hydroxide, and filter. As the ferric hydroxide still contains a small amount of nickel, cobalt and zinc, dissolve the washed precipitate in hydrochloric acid, neutralize with ammonium hydroxide or ammonium carbonate, and precipitate the iron as basic carbonate by boiling. See page 119.

The iron precipitate should be tested for nickel and cobalt, and the precipitation repeated, if necessary.

Separate the zinc from the cobalt and nickel, as given under German Silver. The nickel and cobalt may be precipitated in the filtrate from the zinc sulphide by the addition of ammonium hydroxide and ammonium sulphide.

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* If the arsenic has been eliminated by the method of Piloty, page 93, all the other metals can be determined in the solution remaining in the distilling flask.

Filter, and wash the sulphides of cobalt and nickel, remove as completely as possible from the filter, dry and incinerate the latter, and then dissolve the precipitate and filter ash in hydrochloric acid* with the addition of a little nitric acid. Dilute the solution, transfer to a platinum or porcelain dish and precipitate the cobalt and nickel with potassium hydroxide. Filter, and wash the precipitate with hot water by decantation, and reduce it to metallic cobalt and nickel, by ignition in a current of hydrogen. The reduced metals should be digested with hot water to remove any alkali present, and the ignition repeated. The metals are usually contaminated with silica, ferric oxide and alumina ; dissolve the metals in nitric acid, filter out the silica, and precipitate the iron and alumina with ammonium carbonate, after neutralizing with ammonium hydroxide. After filtration, the precipitate should be dissolved in nitric acid and the precipitation repeated. Evaporate the filtrates to dryness, volatilize the ammonium salts by gentle ignition, and separate the cobalt from the nickel as given on page 33.

The two metals may also be separated by the method of v. Knorre and Illinski, page 36, or according to the Second Method, page 34.

It is best to determine the sulphur in a special sample. See Pyrite, page 210.

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* If manganese is present, first treat the sulphides with a mixture of dilute hydrochloric acid and hydrogen sulphide water. See p. 136.

COPPER OR LEAD SPEISE.

These metallurgical products are obtained by fusing Copper Ores containing Antimony and Arsenic, or Lead Ores containing Nickel and Arsenic. They contain Arsenides or Antimonides of Iron, Cobalt and Nickel, together with Sulphides of Copper, Lead, Silver, Bismuth, Iron and Zinc.

The analysis may be executed as given under Copper Matte. If the speise contains bismuth, it is separated as bismuth oxychloride, in the filtrate from the lead sulphate, after expelling the alcohol; add hydrochloric acid to the solution and dilute largely with water. See page 71.

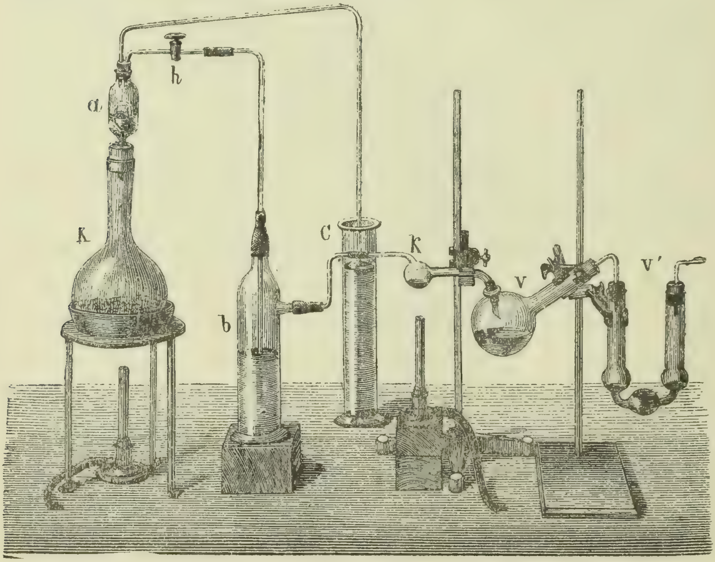

Fig. 41.

The finely divided speise can also be decomposed by chlorine gas; use the apparatus shown in Fig 41.

The bulb-tube k[*], of difficultly fusible glass, contains the substance, and is connected with an apparatus for generating chlorine, and with two absorption flasks, v and v′.

The arm of the bulb-tube bent down, almost touches the liquid in the flask v. The gas generator K, contains coarsely pulverized pyrolusite. The gas[†] evolved by warming the pyrolusite with hydrochloric acid, is dried by passing through concentrated sulphuric acid in the flasks a and b.

In order to regulate the evolution of gas, a glass tube, bent twice at right angles, is connected with the flask K; the other end of the tube is immersed in potassium hydroxide in the cylinder C. By partly or completely closing the stop-cock h, the excess of chlorine may be passed into the potassium hydroxide, and absorbed. v and v′ are partly filled with a mixture of equal volumes of hydrochloric acid and tartaric acid. The outer end of the absorption tube v′ is provided with a glass tube, for connection with a suction pump, or to pass the excess of

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[*] In place of the bulb-tube, the author uses a combustion tube which has been drawn out narrow and bent down. The substance is put in a porcelain boat and shoved into the tube.

Jannasch has constructed a special apparatus for the purpose, shown in Fig. 40. The parts a and b are united by ground glass joints. The bulb-tube, bent down, is connected with the absorption flask v, shown in Fig. 41.

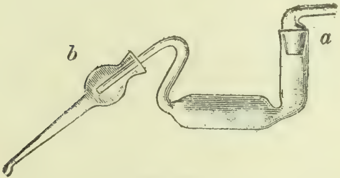

Fig. 40.

[†] The most convenient method for generating chlorine gas for analytical purposes, is to warm potassium bichromate with hydrochloric acid.

chlorine into an absorbent.

As chlorine attacks rubber, cork stoppers should be used, and where rubber tubing must be used for connections, the ends of the glass tubes should fit up tight.

When the apparatus is set up, pass a slow current of chlorine through the bulb-tube as long as decomposition takes place; the bulb-tube should be warmed toward the end of the decomposition.

Increase the current of chlorine, heat the bulb-tube gently at first and gradually increase the temperature, without, however, bringing it to a red heat. The volatile chlorides of arsenic, antimony and a part of the zinc and iron, and the sulphur as chloride, will be driven over into the flasks v and v′, or into the lower end of the bulb-tube; the metallic chlorides pass into solution, while the chloride of sulphur is oxidized to sulphuric acid*.

When no more sublimation of chlorides takes place on further heating the tube, close the stop-cock h, volatilize the substance and drive it over into the absorption flask as completely as possible, by heating with a flame. Cut off the tube behind the bulb, carefully incline the flask v, and dissolve the chlorides adhering to the glass tube.

Transfer the contents of the flasks to a beaker and precipitate the sulphuric acid with barium chloride (page 23). If sulphur has separated in the flask, filter it on a dried and weighed filter, and determine its weight.

After removing the excess of barium chloride with dilute sulphuric acid, precipitate the arsenic and antimony with hydrogen sulphide; separate the sulphides as given on page 89.

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* Under certain conditions the chloride of sulphur is only partly oxidized to sulphuric acid; this may be the case if the substance is so strongly heated with chlorine that chloride of sulphur sublimes before the absorption flasks have been filled with chlorine. The current of chlorine must be regulated by partly closing the stop-cock, and the contents of the bulb should not be too strongly heated at first.

The filtrate from the arsenic and antimony contains some iron and zinc. Precipitate them as sulphides, with ammonium hydroxide and ammonium sulphide*. The sulphides should be filtered without undue exposure to the air and washed with water containing ammonium sulphide. Dissolve the precipitate in hydrochloric acid with the addition of a little nitric acid, and add to the main solution.

Dissolve the non-volatile chlorides of copper, silver, lead, bismuth, cobalt, nickel, iron and zinc, still in the bulb, in dilute hydrochloric acid, and separate them as given in the preceding examples.

PYRARGYRITE. PROUSTITE.

RUBY SILVER ORE.

Silver, Antimony, (Arsenic) Sulphur and Gangue.

The mineral is easily decomposable by chlorine. After decomposition, the bulb-tube contains silver chloride† and gangue, which may be separated as given under Galenite.

For the determination of the elements sublimed into the absorption flask, see the preceding example.

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[*] The filtrate from the sulphide precipitate should not be added directly to the solution of the metals remaining in the bulb-tube k, as the tartaric acid prevents the precipitation of the metals by certain reagents.

[†] The most accurate method of determining silver, is by the method given under Galenite, using a special sample.

TETRAHEDRITE.

GRAY COPPER ORE.

Copper, Antimony, Arsenic, Silver, Lead, Mercury, Iron, Zinc, Sulphur and Gangue.

Chlorine is used for the decomposition. The absorption flask contains antimony, arsenic, and sulphur, as well as iron and zinc.

After separating antimony, arsenic and sulphuric acid, precipitate the iron and zinc with ammonium sulphide; dissolve the precipitate in hydrochloric acid, and proceed as given on page 143. The bulb-tube contains the chlorides of copper, silver and lead, together with the gangue, and under some conditions, iron and zinc. Dissolve the chlorides in dilute hydrochloric acid (the silver chloride and gangue remain insoluble), and separate the metals as given on page 203.

Determination of Mercury:—This determination is best made on a special, large sample, in the 'dry way.'

Place a layer of magnesite about 10 cm. in length in a combustion tube closed at one end, then add a layer of previously dehydrated caustic lime and then a mixture of the sample of tetrahedrite and caustic lime, and finally a layer of pure caustic lime. Stopper the tube with a loose plug of asbestos, draw the tube out to a narrow tube and bend it at a right angle. An ordinary round flask, partly filled with water, is used to receive the mercury. Place the tube in a combustion furnace (see: Organic Analysis), and immerse the point of the tube in the water in the flask. First heat the forward end of the combustion tube and gradually heat the tube its entire length, so that finally the carbon dioxide of the magnesite sweeps the last of the mercury vapor over into the water. While the tube is still hot, cut off the point, rinse into the flask with the wash-bottle, and collect the mercury into one globule by shaking the water. After standing for some time, transfer the mercury to a tared porcelain crucible, remove the water as much as possible with filter paper, and dry the mercury over sulphuric acid in a dessicator.

[Eschka's Method for Mercury*:—This method is especially suitable for low-grade ores, and is both rapid and accurate. The method depends upon distillation of the mercury and catching it on gold in the form of amalgam.

Mix 0.2–2.0 grams of the ore with 1–4 grams of iron filings, in a porcelain crucible of suitable size. Prepare a cover of sheet gold for the crucible; this cover should be in the form of a dish so that it can be kept cool by being filled with water. The cover should be sufficiently large to project some beyond the edge of the crucible, so that no mercury can escape.

Place the weighed cover, filled with cold water, on the crucible containing the ore and iron filings, carefully heat the crucible with a Bunsen burner, keeping the upper part of the crucible cool. Cold water should be added to the cover from time to time. From 10–30 minutes will suffice to distil off the mercury. When the distillation is completed, remove the gold cover, pour off the water, dry carefully, and weigh. The increase in weight of the gold cover represents the weight of the mercury.]

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* [Zeit. f. anal. Chem., Vol. 11, p. 344.]

FURNACE BEARS*.

These accumulations consist principally of Alloys of Iron, together with Copper, Silver, (Gold), Lead, Molybdenum, Vanadium, Cobalt, Nickel and Zinc, with Sulphides, and Phosphides of these metals; they also contain more or less Carbon and Silica.

These substances may be completely decomposed by warming with nitric acid or aqua regia; an insoluble residue of silica and carbon remains. The metals can be separated more easily, however, if the decomposition is effected by chlorine gas. On account of the high percentage of iron, it is necessary to use a tube of hard glass containing 2 bulbs, to avoid stopping the exit tube; the second bulb serving as a sort of condenser for the most of the ferric chloride. Continue heating the substance in the current of chlorine, as long as ferric chloride sublimes, when it is safe to assume that all the molybdenum chloride has been volatilized. The chlorine must be introduced cautiously at first, especially if the substance has been finely pulverized. The flame should be applied only when action in the cold has ceased. After the decomposition, the absorption flask contains the chlorides of sulphur and phosphorus, as well as chlorides of molybdenum, vanadium and iron; the bulb-tube contains the chlorides of the remaining metals, together with the rest of the iron, silica and carbon.

The contents of the absorption flask are used only for the determination of the metals, while sulphur and phosphorus are determined in a special sample. (See below).

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* ["Ofensauen."]

Pass hydrogen sulphide* until the supernatant liquid is perfectly clear.

As the molybdic acid is only gradually changed to sulphide, the solution appears blue even after passing the gas for a long time. On the other hand, the chlorine decomposes a large amount of hydrogen sulphide ; however, it is not advisable to attempt to expel the chlorine, as the dissolved chlorides are very volatile.

Filter the molybdenum sulphide on a filter dried at 100° C., wash it with hot, acidified water, and dry to constant weight at the same temperature. Now heat an aliquot part of the precipitate in a current of hydrogen, and weigh as MoS_2. To avoid partial reduction to metallic molybdenum, use a Bunsen burner, and heat but a short time.

The filtrate from the molybdenum sulphide contains vanadium and iron. Add ammonium hydroxide to alkaline reaction and then yellow ammonium sulphide in excess. After digesting for a long time on the water-bath, all the vanadium will be in solution ; the residue remaining undissolved is ferrous sulphide. Dissolve it in hydrochloric acid, oxidize with nitric acid, precipitate with ammonium hydroxide and weigh as Fe_2O_3.

Determination of Vanadium :—Add acetic acid to the ammonium sulphide solution, to weak acid reaction, expel the hydrogen sulphide by warming, allow to stand for some time and then filter off the vanadium sulphide. Ignite, with access of air, to V_2O_5. See page 162.

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* If the substance does not contain vanadium, saturate the liquid with ammonium hydroxide and ammonium sulphide. Molybdenum is dissolved, while ferrous sulphide remains insoluble.

See Wulfenite. Filter out the ferrous sulphide and ignite to ferric oxide.

Instead of determining the molybdenum and vanadium by the less reliable gravimetric method, the two may be determined volumetrically.

As shown on page 163, vanadic acid is reduced by hydrobromic acid, while molybdic acid is not reduced. If, then, a mixture of the two substances is distilled with potassium bromide and hydrochloric acid, as given on page 163, the amount of the iodine found gives the quantity of vanadic acid present. Let m = equal the number of cc. of thiosulphate used.

If, now, the vanadium tetroxide, V_2O_4, so reduced, is again distilled with potassium iodide and hydrochloric acid, the vanadium is further reduced to vanadium trioxide, V_2O_3:

$$V_2O_4+2HI=V_2O_3+H_2O+I_2,$$

and the equation shows that the same quantity of iodine is liberated as in the first reduction.

If, in the last reduction, molybdic acid is also present, it will be reduced to Mo_2O_5, as given under Wulfenite, if an excess of potassium iodide is present, and a quantity of iodine corresponding to the trioxide will be liberated.

If n cc. of thiosulphide were used to titrate the total iodine that was liberated by the reduction of V_2O_4 and MoO_3, then, (n–m) cc. corresponds to the quantity of molybdenum trioxide present.

The analysis, therefore, is conducted as follows: The weighed vanadate and molybdate are first distilled with potassium bromide and hydrochloric acid, as given on page 163, and the liberated iodine titrated. The amount of vanadium is thus obtained from the quantity m.

Now add to the cooled, blue solution in the distilling flask, about 1 gram of solid potassium iodide and 1–2 cc.

of glacial phosphoric acid, and distil according to the method given under Wulfenite, until all the free iodine is driven over. The amount of thiosulphate used in this titration gives the quantity n; with the aid of the difference, n–m, calculate the molybdic acid according to the equation given under Wulfenite.

To apply this method to the analysis of furnace bears, fuse the substance with an equal weight of potassium nitrate for 1 hour in a silver crucible. Extract the fuse with water, decompose the nitrates by evaporation with hydrochloric acid, and then distil the vanadate and molybdate as given above, after expelling the chlorine and the oxides of nitrogen.

Dissolve the chlorides in the bulb-tube in hydrochloric acid, and filter the carbon on an asbestos filter. Mix the dry carbon with copper oxide and oxidize in a current of oxygen in a combustion tube; the carbon dioxide is absorbed in a soda-lime U-tube, and weighed. For details, see Organic Analysis.

Silver, if present, remains with the carbon. If it is desired to determine the silver as well as the carbon, in the same sample, ignite the residue in the bulb-tube in a current of hydrogen. The silver chloride is reduced to metallic silver, and may be dissolved in dilute nitric acid. After filtering out the carbon, the silver may be precipitated in the filtrate as silver chloride.

The separation of the chlorides dissolved in hydrochloric acid, derived from the non-volatile residue in the bulb-tube, follows from what has been given above.

Determination of Sulphuric Acid:—Dissolve a separate portion of substance in nitric acid or aqua regia, remove the nitric acid by repeated evaporation with hydrochloric acid, and precipitate the sulphuric acid with barium chloride.

Determination of Phosphoric Acid:—Saturate the nitric acid solution of the substance with sodium carbonate, evaporate to dryness, and fuse the residue in a silver or platinum crucible with an equal weight of a mixture of potassium nitrate and sodium carbonate.

Dissolve the fuse in water, saturate with ammonium sulphide, and digest for some time on the water-bath. Molybdenum sulphide is dissolved, and is reprecipitated on the addition of hydrochloric acid. Heat the acidified liquid until it no longer smells of hydrogen sulphide, neutralize with ammonium hydroxide, and precipitate the phosphoric acid with magnesium chloride solution.

All the vanadic acid is in the filtrate from the ammonium-magnesium phosphate, provided a sufficient excess of hydrochloric acid was used to decompose the ammonium sulphide solution.

STIBNITE.

Antimony, Sulphur, (Iron, Lead, Copper and Arsenic).

Various methods may be used for analyzing the mineral. By heating the finely pulverized mineral with dehydrated sodium thiosulphate, and extracting the fuse with water, antimony and arsenic are separated from the remaining metals, which are in the form of insoluble sulphides.

To separate arsenic and antimony, proceed according to Bunsen's method, given under Alloy of Arsenic and Antimony, page 90; the separation of lead, copper, etc., has been given in detail in other places. Sulphur is best determined in a separate sample; add tartaric acid before precipitating with barium chloride, to prevent the precipitation of antimony oxide with the barium sulphate.

The mineral may also be decomposed by chlorine gas. The chlorides of antimony, arsenic, sulphur and iron are sublimed and determined as given under Copper and Lead Speise.

As stibnite is decomposed by chlorine even at the ordinary temperature, the current of gas must be regulated so as to pass very slowly at first, to avoid too rapid sublimation of sulphur chloride. See page 224, note*.

The bulb-tube contains the chlorides of lead, copper, and the remainder of the iron; dissolve them in dilute hydrochloric acid, and separate the lead and copper as given on page 63. Precipitate the iron as hydroxide, in the filtrate from the copper sulphide.

Oftentimes, in the analysis of antimony ores, the determination of antimony alone is required; the determination may be made either gravimetrically or volumetrically. The gravimetric method has been given above. It should be remembered that by heating the mineral with dehydrated sodium thiosulphate or a mixture of sodium carbonate and sulphur, and digesting in water, the antimony passes into solution as a double salt, and is precipitated as antimony sulphide, on the addition of dilute sulphuric acid. The sulphide may be weighed as such, or the antimony may be calculated from the hydrogen sulphide evolved when the sulphide is boiled with dilute hydrochloride acid. See page 80.

The volumetric determination of antimony depends upon the fact that antimonous acid is oxidized by iodine in alkaline solution to antimonic acid:

$$HSbO_2+I_2+H_2O=HSbO_3+2HI.$$

Dissolve the antimony sulphide in hydrochloric acid, warm until the solution no longer smells of hydrogen sulphide, filter out the free sulphur, add tartaric acid or potassium-sodium tartrate, and then add sodium bicarbonate in excess. After addition of starch solution, titrate with iodine to the end reaction. See Volumetric Analysis: Sodium Arsenite and Iodine.

BOURNONITE.

Antimony, Lead, Copper, (Iron), and Sulphur.

Decompose the finely pulverized mineral with chlorine gas, and proceed as given above.

ZINKENITE.

Antimony, Lead, (Silver, Copper, Iron), and Sulphur.

Decompose as given above. As the zinkenite, with the exception of the silver, is completely decomposed by hydrochloric acid, the metals may be determined in the solution. The silver remains insoluble as silver chloride.

According to Woehler, all the sulphur of zinkenite is evolved as hydrogen sulphide, on igniting the mineral in a current of hydrogen, and the other constituents remain behind. The analysis may be made as follows: Place a weighed amount of the substance in a porcelain boat, and ignite in a current of hydrogen in a combustion tube. Conduct the hydrogen sulphide and excess of hydrogen into an ammoniacal solution of hydrogen peroxide, or into bromine solution, (page 181); precipitate as barium sulphate, and calculate the sulphur. After complete decomposition, dissolve the residue in the boat in a mixture of nitric acid and tartaric acid, and determine the metals as given above.

ULLMANNITE.

Antimony, Nickel and Sulphur.

The mineral is decomposable by chlorine gas. Dissolve the nickelous chloride, remaining in the bulb, in dilute hydrochloric acid, and precipitate the nickel with potassium hydroxide. Reduce the nickelous hydroxide to metallic nickel in a current of hydrogen.

NICCOLITE.

Nickel, Arsenic, (Iron, Lead and Sulphur).

Dissolve the finely pulverized mineral in aqua regia, and remove the nitric acid by evaporation with hydrochloric acid. Precipitate the arsenic from the hydrochloric acid solution, by passing hydrogen sulphide. If other metals of the hydrogen sulphide group are present, separate them with sodium sulphide.

Separate the nickel from the iron, in the filtrate, as given on page 69.

Determine the sulphur in a special sample, by oxidation with nitric acid or aqua regia, and precipitation with barium chloride.

It is probably unnecessary to mention that the arsenic may be separated by volatilization, as arsenous chloride, and then determined as given on page 93 ; the lead, nickel and iron may then be separated and determined in the residue remaining in the distilling flask.

LINNÆITE.

Constituents : Cobalt and Sulphur.

Decompose the finely pulverized mineral with aqua regia, and heat on the sand-bath until the sulphuric acid is expelled.

Determine the cobalt as given on page 33. Determine the sulphur as given in the preceding example.

COBALTITE.

Cobalt, Iron, (Copper, Antimony), Arsenic and Sulphur.

The method follows from the preceding examples.

See : e. g., Nickel Matte.

GLAUCODOTE.

Cobalt, Iron, Arsenic and Sulphur.

The analysis may be made as given under Cobaltite.

CERUSSITE.

Lead, (Iron, Calcium), and Carbon Dioxide.

Pulverize the mineral, and dry at 100° C. Dissolve a sample in dilute nitric acid, and precipitate the lead either as sulphate or as sulphide. If the lead is precipitated as sulphide, oxidize the filtrate with nitric acid, and precipitate the iron and calcium, as usual.

Determine the carbon dioxide in a special sample. See page 56.

GALENITE.

Lead, (Antimony, Arsenic, Copper, Silver, Gold, Zinc, Iron), Sulphur, and Gangue.

Galenite rich in antimony, is most easily decomposed by chlorine gas. If the ore contains antimony, and nitric acid or other oxidizing agent is used as a solvent, the lead sulphate is always contaminated with antimony. For this reason, use a mixture of nitric acid and tartaric acid ; the method is described under Type Metal, page 78.

After decomposition with chlorine gas, the absorption flask will contain sulphuric acid, antimony, and arsenic, together with a portion of the iron and zinc. These may be separated as given on gage 219.

The bulb-tube contains the chlorides of lead, silver, copper and the remainder of the iron and zinc. Their separation can likewise be found described above, and the method need be given only in outline at this place.

Dissolve the contents of the bulb in dilute hydrochloric acid ; the greater part of the lead separates as lead chloride, and is dissolved only by repeated boiling with water. The insoluble residue is silver chloride and gangue*. First separate the lead by evaporation with sulphuric acid, filter, and precipitate the copper in the filtrate with hydrogen sulphide. After expelling the hydrogen sulphide, separate the iron from the zinc as given under Sphalerite.

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* The silver is generally determined by assay, on a special sample. See page 239. To determine the gangue and silver chloride, ignite the residue in a current of hydrogen, which forms metallic silver and a compound of silver and silicon. By warming the residue with dilute nitric acid, all the silver is dissolved. The silica or gangue is then completely separated by evaporation on the water-bath. The filtrate from the silica may be used for the determination of silver.

If galenite is decomposed with strong nitric acid, the most of the lead separates as lead sulphate. This can be dissolved by warming with hydrochloric acid, and can then be separated from the gangue. The nitric acid solution can also be evaporated with sulphuric acid, and the lead completely separated as sulphate. In the latter case, determine the weight of the lead sulphate and silica, and then digest with a solution of ammonium acetate or ammonium tartrate.

This completely dissolves the lead sulphate. Weigh the insoluble matter, and calculate the lead sulphate by difference. The lead may also be determined as follows: Pour the hot hydrochloric acid solution, or the ammonium acetate solution, of the lead sulphate into a mixture of 25 cc. of water, 50–100 cc. of 3% hydrogen peroxide, and 50 cc. of concentrated ammonium hydroxide. Allow the precipitate of PbO_2 to stand for 6–8 hours, with occasional stirring; filter, wash with cold water, and ignite to lead oxide, PbO, in a porcelain crucible.

The other metals are contained in the filtrate from the lead, and may be determined by the methods given above.

In an ordinary analysis of galenite, only silver and lead are determined. For this purpose, the following method is used almost exclusively.

Mix 25 grams of the pulverized ore with 2–3 times the amount of sodium carbonate, place in an iron, sand or clay crucible, cover with borax and place either in a hot muffle of an assay furnace, or in a coke furnace. When the contents of the crucible are liquid, close the draught, which causes the temperature to fall. Allow the crucible to remain in the furnace about 10–20 minutes longer, depending upon the fusibility of the gangue in the ore. When the charge is in quiet fusion, remove the crucible from the furnace and tap it on the floor to unite the lead into one button, and pour the slag and lead into a scorification mould. With a little care it is easy to obtain a button of lead free from slag, which may be weighed direct. If the button contains slag, remove it by hammering and washing; the clean button may then be weighed.

The reduced lead contains all the silver contained in the sample. To determine the silver, the lead is first oxidized to lead oxide, by heating in an oxidizing atmosphere. Place the lead button in a previously heated cupel, in a hot muffle. As soon as the lead is melted, the draught must be partly shut off, to moderate the temperature; otherwise a part of the silver may be oxidized, and absorbed in the cupel. On the other hand, the temperature should not be allowed to fall sufficient to 'freeze' the button. If the button once solidifies before all the lead is oxidized, it is difficult to finish the process.

It is easily seen when all the lead is removed; in place of the thin layer of lead oxide on the molten button, the white color of the silver may be seen. Take the cupel from the muffle, and remove the adhering lead oxide from the silver button while still warm, by flattening it out on a steel anvil.

If the galenite contains gold, it will be contained in the silver button. Dissolve the silver in dilute nitric acid, in a weighed porcelain crucible, wash the residual gold with hot water by decantation, ignite gently, and weigh.

The determination of sulphur in galenite may be made in various ways. Heat the finely powdered substance with a large excess of concentrated hydrochloric acid, in the apparatus shown on page 181, oxidize the hydrogen sulphide evolved, and determine as barium sulphate.

The substance may also be decomposed by fusion in a porcelain or platinum crucible with 6 parts of sodium carbonate and 4 parts of potassium nitrate*.

Dissolve the fused mass in water, separate the lead in solution by passing a current of carbon dioxide, and filter. Evaporate the filtrate repeatedly with addition of hydrochloric acid, and precipitate the sulphuric acid with barium chloride.

If the lead is separated by hydrogen peroxide, as described above, the sulphur can be determined in the same sample, if care is taken to effect complete oxidation of the sulphur. Digest the powdered mineral for a short time with dilute nitric acid at the ordinary temperature, add concentrated nitric acid, gradually warm, and finally evaporate to dryness on the water-bath. If free sulphur separates, warm again with nitric acid, with a few drops of bromine, and repeat this treatment until all the sulphur is oxidized. Finally evaporate to dryness with nitric acid, dissolve the lead sulphate in a boiling mixture of 3 parts water and 2 parts hydrochloric acid, filter out the gangue, and pour the solution into the ammoniacal hydrogen peroxide solution described above.

Heat the filtrate from the lead precipitate, to expel the ammonia, then add hydrochloric acid and alcohol, and heat again to destroy the hydrogen peroxide and decompose the persulphuric acid; finally precipitate with barium chloride.

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* The crucible will be somewhat attacked by the molten flux.

WULFENITE.

Lead Molybdate.

The mineral may easily be decomposed by fusion with a mixture of equal parts of sodium carbonate and sulphur. The water solution of the fused mass contains the molybdenum in the form of sodium sulpho-molybdate. This compound is decomposed on the addition of hydrochloric acid, and molybdenum sulphide is precipitated. The decomposition is best effected in a boiling solution; boil until all the hydrogen sulphide is volatilized.

Filter the molybdenum sulphide on a filter that has been dried at 120° C., and weighed, wash the precipitate with hot water, and dry at the same temperature. Ignite an aliquot part of the precipitate in a current of hydrogen, and weigh as MoS_2. See page 229.

Volumetric Determination of Molybdenum:—This method depends upon the reduction of molybdenum trioxide by hydriodic acid, and titration of the liberated iodine, with sodium thiosulphate. See: Volumetric Analysis. Hydrochloric acid and hydrobromic acid do not react in the same manner, to liberate the corresponding halogen.

According to the equation,

$$2MoO_3+2HI=Mo_2O_5+H_2O+I_2,$$

1 molecule of iodine corresponds in 2 molecules of molybdenum trioxide.

Place about 0.2–0.3 gram of the molybdate, together with about 0.5 gram of potassium iodide, in the distilling flask of Bunsen's apparatus*, and add sufficient hydrochloric acid, Sp. Gr. 1.12, to fill the flask about 2/3 full.

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* See: Volumetric Analysis.

The heating must be slow enough to fill the exit tube with iodine vapor, before the contents of the flask boil. Hydriodic acid should not be generated as long as there is any air in the flask, as it may be decomposed, liberating free iodine. The air should be replaced by carbon dioxide. As soon as all the iodine vapor has been distilled over and absorbed by the potassium iodide, titrate with sodium thiosulphate.

To determine molybdenum in wulfenite, by this method, dissolve the pulverized mineral in dilute nitric acid, nearly neutralize with ammonium hydroxide and add yellow ammonium sulphide. Digest for some time on the water-bath. After the molybdenum sulphide has dissolved, and the lead sulphide has settled, filter, and reprecipitate the molybdenum as sulphide, by the addition of hydrochloric acid, Oxidize the molybdenum sulphide with potassium chlorate, heat, to volatilize the free chlorine, and distil as given above.

Wash the lead sulphide with water containing hydrogen sulphide, and determine it as such. See page 44.

PYROMORPHITE.

GREEN OR BROWN LEAD ORE.

Lead Phosphate and Lead Chloride; occasionally with Lead Sulphate, together with Lead Arsenate and Calcium Fluoride.

Determination of Lead, Calcium, Phosphoric Acid and Arsenic Acid:—Digest the powdered mineral with nitric acid, until in complete solution, add hydrochloric acid and evaporate on the water-bath. As nitric acid is detrimental to the precipitation of arsenic acid by hydrogen sulphide, it is necessary to repeat the evaporation with hydrochloric acid. Dissolve the residue as completely as possible in hydrochloric acid, decant the clear solution, dissolve the lead chloride by boiling with water, and pass a current of hydrogen sulphide. Digest the precipitate of arsenic sulphide and lead sulphide, in ammonium sulphide or sodium sulphide, and determine the insoluble lead sulphide by igniting in a current of hydrogen and weighing. The arsenic may be reprecipitated as sulphide, by the addition of dilute hydrochloric acid. Oxidize the arsenic sulphide with nitric acid, and determine the arsenic as pyroarsenate.

Add dilute sulphuric acid to the filtrate from the hydrogen sulphide precipitate, and concentrate on the water-bath to volatilize the hydrochloric acid; this precipitates the calcium as sulphate. Add alcohol to decrease the solubility, filter, wash the calcium sulphate with alcohol, ignite and weigh.

Neutralize the filtrate with ammonium hydroxide, and precipitate the phosphoric acid with magnesium chloride solution. As the precipitate may be contaminated with sulphuric acid, it is necessary to dissolve the washed precipitate in hydrochloric acid, and repeat the precipitation with ammonium hydroxide and a few drops of magnesium solution.

Determine the chlorine as given on page 158.

For the sulphuric acid determination, dissolve a separate sample, and precipitate with barium chloride, after evaporating off the excess of the hydrochloric acid.

See pages 150 and 153, for the Determination of Fluorine.

LEAD MATTE.

Lead, Copper, Iron, (Silver, Antimony, Nickel, Zinc), and Sulphur.

Decompose the finely pulverized substance with chloine gas, and proceed as given on page 222.

RED LEAD.

Commercial Red Lead consists principally of Lead Tetroxide, together with small amounts of Arsenic, (Antimony), Copper. Silver, Iron, Zinc, Calcium, Silica and Carbon Dioxide.

If the lead monoxide was not completely oxidized, the commercial red lead contains more or less unchanged lead monoxide. To determine the latter, pulverize and dry the substance, and digest a sample with a solution of neutral lead acetate, in which the lead monoxide is completely soluble. Filter out the insoluble lead tetroxide on a weighed filter dried at 100° C., and dry to constant weight at the same temperature.

Determination of Impurities in Red Lead:—Dissolve a weighed sample of the dry substance in hydrochloric acid; if lead chloride separates out, it may be dissolved by repeated treatment with hot water. Silica, and silver in the form of chloride, if the latter metal was present, will be insoluble*. Filter out the insoluble matter, and precipitate the lead in the filtrate, by evaporation with sulphuric acid.

Arsenic, antimony and copper may be present in small quantities; pass hydrogen sulphide through the filtrate from the lead sulphate, and separate the arsenic and antimony from the copper, with sodium sulphide, and determine as given on page 89. Wash the insoluble copper sulphide with water containing hydrogen sulphide, ignite in a current of hydrogen, and weigh.

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* Silica and silver chloride may be separated by the method given on page 233.

Determine iron, zinc and calcium as usual in the filtrate from the hydrogen sulphide precipitate.

To determine silver, at least 25 grams of the red lead should be taken. Fuse with soda and borax, and treat the lead button as given on page 239.

Carbon dioxide may be determined ae given on page 56. As lead tetroxide and hydrochloric acid react to form lead chloride and chlorine, sulphuric acid should be used for the decomposition.

Lux has based a method for the valuation of red lead upon the titration of the lead dioxide with standard oxalic acid, and the titration of the total lead with standard potassium bichromate.

Lead dioxide reacts with oxalic acid as follows:

$$PbO_2 + H_2C_2O_4 = PbO + 2CO_2 + H_2O.$$

Digest 2.07 grams of the red lead in a large porcelain dish, with 20–30 cc. of dilute nitric acid. After a few minutes the red lead will be decomposed into insoluble lead dioxide and soluble lead nitrate. Now add 50 cc. of fifth-normal oxalic acid* and boil. The lead dioxide soon dissolves, while the impurities, sand, barium sulphate and lead sulphate, remain insoluble. Without filtering, titrate the excess of oxalic acid with a standard solution of potassium permanganate of about the same strength. As the oxidation of oxalic acid is slow in nitric acid solution, add

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* See: Volumetric Analysis.

5–10 cc. of permanganate at once; the titration may now be continued as usual. Toward the end of the titration, it is necessary to heat the solution for about half a minute, to be sure that the oxidation is complete.

Subtract the number of cc. of permanganate used, from the total number of cc. of oxalic acid used, and the remainder corresponds to the lead dioxide present.

The lead monoxide may be determined by titrating the total lead, and subtracting the lead dioxide found. Reduce the slight excess of permanganate by the addition of a few drops of oxalic acid, neutralize with ammonium hydroxide and add sodium acetate in excess. Titrate the lead with a solution of potassium bichromate containing 14.761 grams of $K_2Cr_2O_7$ in a liter. Each cc. of this solusolution corresponds to 1% of lead.

CINNABAR.*

Mercuric Sulphide; also contains Iron, Manganese, (Copper), Aluminum and Calcium.

Determination of Sulphur:—The sulphur can be oxidized to sulphuric acid with aqua regia, with nitric acid and potassium chlorate, or with bromine solution. Another method depends upon the oxidation of sulphur by chlorine gas in the presence of potassium or sodium hydroxide. Suspend the finely pulverized substance in dilute potassium or sodium hydroxide, warm, and pass chlorine until the red color of the cinnabar has disappeared, and brownish-red mercuric oxide is formed; or, continue the passage of chlorine until all the mercury is in the form of the white chloride. After acidifying with hydrochloric acid, determine the sulphuric acid as usual.

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* For the electrolytic determination of mercury, see Foot Note p. 1.

Determination of Mercury and the other Metals :—Dissolve a sample in aqua regia; add hydrochloric acid, and evaporate to dryness on the water-bath. Dissolve the residue in hydrochloric acid, add sulphurous acid, and boil, to reduce the iron to the ferrous condition. Precipitate the mercury with hydrogen sulphide, filter on a filter that has been dried at 100° C. and weighed. Wash the precipitate with water, and dry to constant weight at the same temperature. Weigh as HgS.

If the reduction with sulphurous acid was omitted, or incomplete, the mercuric sulphide will be contaminated with sulphur. To remove the latter, wash the precipitate 8 times with alcohol, 4 times with carbon bisulphide and finally 3 times with alcohol. If the precipitate contains a large amount of sulphur, it is expedient to dissolve it with sodium sulphite. Lay the filter on a glass plate, rinse the precipitate into a porcelain dish, and warm with sodium sulphite. Dry the filter, fold again, and filter off the mercuric sulphide, wash with cold water and dry, as given above.

This method is not applicable in the presence of copper, as the latter element is not completely separated from the mercury. In this case, add an excess of phosphorous acid to the hydrochloric acid solution ; this reduces the mercuric chloride to insoluble mercurous chloride. After standing for 12 hours in a moderately warm place, filter off the precipitate on a dried and weighed filter, wash with hot water, and dry at the same temperature, to constant weight.

Determine the copper in the filtrate, as given on page 64.

The filtrate from the cuprous sulphide contains the remaining metals; for their separation, see page 111 *et seq.*

If it is desired to determine mercury only, in mercury ores, the 'dry way' given on page 226, may be used, or the mercury may be determined in the 'wet way,' by reduction to metallic mercury with stannous chloride.

Reduction with Stannous Chloride:—Dissolve the ore in aqua regia, evaporate to dryness, and repeat the evaporation with hydrochloric acid to expel all of the nitric acid. Add an excess of a clear solution of stannous chloride, obtained by dissolving tin in hydrochloric acid, and heat to boiling. The mercuric chloride is quantitatively reduced to metallic mercury, with the formation of stannic chloride. When the precipitate has settled, decant the clear liquid, and unite the finely divided mercury into one globule by heating with a little stannous chloride and a few drops of hydrochloric acid.

Wash the mercury by decantation with water containing a little hydrochloric acid, and then with pure water, and transfer to a tared porcelain crucible. Remove the greater part of the adhering water with filter paper, and then place the crucible in a dessicator containing concentrated sulphuric acid. When perfectly dry, weigh as metallic mercury.

If the cinnabar contains appreciable amounts of other metallic compounds, it is preferable to decompose the ore with chlorine; the mercury will be volatilized as mercuric chloride and retained by the absorption flask.

Some samples of cinnabar contain carbonaceous matter, and their solutions either clog the filter, or give turbid filtrates. Such ores are best decomposed by heating in a current of oxygen, in the apparatus described by Jannasch*. The oxidation product of sulphur, and the metallic mercury, are retained in a flask containing dilute nitric acid. After all the mercury has dissolved, evaporate the solution to dryness, and dissolve the residue in hydrochloric acid and water. Precipitate the sulphuric acid by a very slight excess of barium chloride, remove the excess by sulphuric acid, and precipitate the mercury with hydrogen sulphide, as given above.

To determine the carbon in the carbonaceous matter, ignite a special sample of the cinnabar in the manner above described, but retain the mercury in a U-tube filled with glass wool; following the U-tube, is a straight tube filled with a mixture of lead monoxide and lead dioxide, to absorb sulphur trioxide and sulphur dioxide. After the carbon dioxide has passed through a calcium chloride tube to dry it, it is absorbed in a soda-lime tube, and then weighed.

MOLYBDENITE.

Molybdenum Sulphide.

The mineral can be decomposed by fusion with sodium carbonate and sulphur. Dissolve the fused mass in water, and precipitate the molybdenum sulphide by the addition of hydrochloric acid. Determine the molybdenum sulphide as given on page 229.

If the molybdenite contains other metals, their sulphides will remain insoluble when the fuse is dissolved in water.

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* Page 223.

Determination of Sulphur:—Fuse a sample with a mixture of sodium carbonate and potassium chlorate, as given on page 211.

BISMUTHINITE.

Bismuth, (Copper, Lead, Gold, Tellurium, Arsenic, Iron, Cobalt, Nickel), and Sulphur.

The mineral can be decomposed by digestion with concentrated nitric acid. If the mineral contains insoluble matter, it should be tested for gold; treat the residue with aqua regia and proceed as given on page 212. After evaporating the excess of nitric acid on the water-bath, add hydrochloric acid and dilute with water; bismuth oxychloride is precipitated. Treat it as given on page 73.

The filtrate contains the remaining metals. To determine tellurium, evaporate the nitric acid, dissolve the residue in dilute hydrochloric acid, and separate the tellurium in the elemental form by heating with an excess of sulphur dioxide or potassium bisulphite. If the solution is dilute, or only a small amount of tellurium is present, the solution must be allowed to stand for several days in a warm place, for complete precipitation. Wash the tellurium by decantation with water containing sulphur dioxide, filter on a dried and weighed filter, and dry to constant weight at 100° C.

Gold, if in solution, will be precipitated with the tellurium. Treat the weighed precipitate with nitric acid; the tellurium is dissolved, and the residual gold can be weighed. Or, dissolve both metals in aqua regia, remove the nitric acid by evaporation, and reduce the hydrochloric acid solution with a concentrated solution of ferrous sulphate, which precipitates the gold and does not reduce the tellurium.

The separation of the remaining metals, in the filtrate from the gold and tellurium, follows from what has preceded.

URANINITE*.

PITCH BLENDE.

Uranate of Uranyl, with varying proportions of Lead, Copper, Bismuth, Arsenic, Antimony, Sulphur, Selenium, Vanadium, Iron, Manganese, Cobalt, Nickel, Zinc, Calcium, Magnesium, Sodium, Carbon Dioxide, Silica and Water†.

If the mineral contains selenium, the best method for its determination is to heat the finely pulverized substance in a current of chlorine; this volatilizes the selenium as chloride, together with the chlorides of bismuth, arsenic, antimony, sulphur, vanadium and iron. After complete decomposition, warm the liquid in the absorption flask to remove the chlorine, and precipitate the selenium by reduction with sulphur dioxide or potassium bisulphite. Proceed exactly as given in the Determination of Tellurium, page 250.

The vanadium is likewise best determined in a special sample. Fuse the finely ground substance in a silver crucible for about an hour with an equal weight of potassium nitrate. Extract the fuse with water, which dissolves the vanadium as potassium vanadate. Add hydrochloric acid, evaporate to dryness to expel the nitric acid, dissolve the residue in hydrochloric acid and reduce the selenium with sulphur dioxide. The selenium, separated at this point, may serve as a check on the original determination.

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* [Compare: Hillebrand, Bull. 78, U. S. Geol. Surv., and Ramsey and Travers, Proc. Royal Soc. 1897, Vol. 60, pp. 442–448.]

† Cl. Zimmerman has found thallium in commercial uranium oxides. This element must therefore be a constituent of the mineral.

Boil off the sulphur dioxide, oxidize the solution with potassium chlorate, evaporate several times with hydrochloric acid to remove the free chlorine, and determine the vanadium volumetrically with iodine, as given on page 163.

Determination of the other Metals:—Digest a sample of the finely powdered mineral with nitric acid. If a portion of the mineral remains insoluble, decompose it by warming with a mixture of nitric acid and sulphuric acid, and filter out the silica. After removing the excess of acid, precipitate the hydrogen sulphide group of metals by passing the gas. Separate arsenic and antimony (selenium) by digesting the sulphides with ammonium sulphide, or with sodium sulphide if copper is present. Dissolve the insoluble sulphides in nitric acid, and separate bismuth and lead as given on page 71. The filtrate from the bismuth oxychloride contains the copper, which may be determined as sulphide or sulphocyanate.

Neutralize the filtrate from the sulphide precipitate with ammonium hydroxide, add ammonium sulphide, dissolve the remaining precipitate in hydrochloric acid with the addition of a little nitric acid, and precipitate the iron and uranium with ammonium hydroxide. To remove the cobalt and nickel precipitated with the iron and uranium, it is necessary to dissolve the washed precipitate in hydrochloric acid and repeat the precipitation with ammonium hydroxide. To separate the iron and uranium, dry the precipitate and ignite it in a current of hydrogen, which reduces the iron to the metallic state and the uranium to uranous oxide. On treating the residue with dilute hydrochloric acid, the iron dissolves. Re-ignite the insoluble uranous oxide, UO_2, in hydrogen, and weigh as such.

The mixture of iron and uranium can also be heated in a current of dry hydrochloric acid ; the iron volatilizes as ferrous chloride.

Sweep the hydrochloric acid from the apparatus by passing hydrogen for a few hours, and determine the weight of the UO_2.

If chromium is present, it will be found with the uranous oxide. Warm the mixture with dilute nitric acid, filter off the insoluble chromic oxide, wash with hot water and weigh.

The separation and determination of the remaining metals has been given above.

Determine carbon dioxide and sulphur in special samples, the former as given under Dolomite, and the latter according to the method given under Ultramarine, or Pyrite.

If the mineral evolves hydrogen sulphide when treated with an acid, interpose 2 U-tubes filled with pumice stone saturated with copper sulphate, and calcium chloride, between the sulphuric acid drying tube and the soda-lime tube. The pumice stone is prepared as follows : Pour a hot, concentrated solution of copper sulphate over pieces of pumice the size of a pea (30 grams copper sulphate : 60 grams pumice) and evaporate to dryness. Heat the dry mass for about 4 hours at 150–160° C. and preserve in a stoppered bottle. Fill the two U-tubes 5/6 with the prepared pumice, and the remainder with calcium chloride.

WOLFRAMITE.

Tungstic Acid, Iron, Manganese, (Calcium, Magnesium, Tin, Silica).

Dry 3–5 grams of the finely pulverized mineral at 110° C. The mineral is difficultly decomposable by digestion with acids, but is easily decomposed by fusion with 4 times its weight of potassium-sodium carbonate. Dissolve the fused mass in boiling water; the tungsten goes into solution as potassium or sodium tungstate.

Iron, Manganese, etc., remain insoluble. Wash the insoluble matter with hot water, dissolve in hydrochloric acid, and separate the metals as given on page 119.

The tungstic acid may be separated, as such, from the alkaline solution, or it may be separated as mercurous tungstate.

To separate the tungstic acid as such from the alkaline solution, acidify the latter with hydrochloric acid, evaporate to dryness on the water-bath and heat the residue for some time at 120° C. Dissolve the alkaline chlorides in water, add a little hydrochloric acid, filter out the tungstic acid, wash it with hot water containing hydrochloric acid, and ignite with access of air. To avoid reducing the tungstic acid by the carbon of the filter paper, remove the precipitate as much as possible from the filter, moisten the paper with ammonium nitrate, dry, and incinerate over the crucible in a coil of platinum wire. If the ignited tungstic acid is not pure yellow, moisten it with a few drops of nitric acid and repeat the ignition in an open crucible.

Precipitation as Mercurous Tungstate:—Add dilute nitric acid, to slightly acid reaction, warm, to expel ababsorbed carbon dioxide, and proceed as given at the end of this analysis.

The ignited tungstic acid may contain silica and stannic oxide. The former may be removed by warming with a few cc. of hydrofluoric acid, evaporating to dryness and igniting. The residue consists of pure tungstic acid, or tungstic acid and stannic oxide. In the latter case, volatilize the tin as stannic chloride, by igniting with ammonium chloride. The stannic chloride is decomposed by the moisture of the air, and stannic oxide may be deposited on the outside of the crucible. To prevent this, place the crucible in a larger crucible, and keep the outer crucible covered during the ignition.

Repeat the ignition several times with 6–8 times as much ammonium chloride as there is precipitate, until the weight of the residual tungstic acid is constant. The tungstic acid becomes dark on igniting in the absence of air, and only assumes its true color and weight on igniting with access of air.

The volatilization of large quantities of stannic oxide requires considerable time. If, therefore, it is necessary to make a separation of tungsten from tin, it is best to proceed as follows: Mix the two oxides, such as would be obtained, for example, in the oxidation of a tungsten bronze by nitric acid, and carefully ignite for 15 minutes in a small covered porcelain crucible with twice the volume of zinc dust or zinc filings. Transfer the mass to a beaker, add hydrochloric acid, (1 part acid : 2 parts water) and heat to boiling; boil until no more hydrogen is evolved. Cool the solution somewhat and add potassium chlorate in small portions until the blue tungstic oxide is oxidized to yellow tungstic acid and the blue color has disappeared. Dilute the solution with 1.5 times its volume of water, and allow to stand 24 hours. Filter out the tungstic acid, wash first with water containing nitric acid, and then with a dilute, hot solution of ammonium nitrate, as pure water causes the precipitate to run through the filter. Ignite and weigh as WoO_3.

Direct Determination of Tin :—Pass hydrogen sulphide through the filtrate from the tungstic acid, filter out the stannic sulphide, and ignite to stannic oxide.

Another method for separating tungsten and tin, depends upon the reduction of stannic oxide to metallic tin by fused potassium cyanide ; the tungsten trioxide forms potassium tungstate, which dissolves when the cooled fuse is digested in water. The method is exactly the same as that given for the separation of phosphoric acid and tin, page 85. The metallic tin is oxidized by nitric acid to stannic oxide, and weighed as such.

To precipitate the tungstic acid, add nitric acid to the potassium cyanide solution, to weakly acid reaction. Remove the hydrocyanic acid by warming* and add a sufficient amount of mercurous nitrate. Now add ammonium hydroxide, drop by drop, until the precipitate assumes a brown color. Allow the precipitate to settle, filter, and wash with water containing mercurous nitrate. Ignite with access of air, and weigh as WoO_3.

If the mineral contains molybdenum, it will be precipitated as trioxide, with the tungstic acid. In this case, ignite the mercurous nitrate precipitate as given above, dissolve the oxides in ammonium hydroxide, add tartaric acid and hydrochloric acid and precipitate the molybdenum with hydrogen sulphide.

Evaporate the filtrate to dryness, to separate the tungstic acid, and ignite the residue.

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* [This operation should be performed in a hood with a good draught as the fumes are very poisonous.]

SCHEELITE.

Calcium Tungstate, occasionally with small amounts of Magnesium and Copper.

Scheelite is completely decomposable by hydrochloric acid or nitric acid. Evaporate the solution to dryness, heat the residue at 120° C., and add dilute hydrochloric acid. Treat the insoluble tungstic acid as given above.

Determine calcium and magnesium, as usual, in the filtrate from the tungstic acid. If the mineral contains copper, first separate it by passing hydrogen sulphide.

REFINED LEAD.

Lead, with small amounts of Silver, Copper, Bismuth, Antimony, (Arsenic), Cadmium, Iron, Zinc, Nickel, (Cobalt, and Manganese).

Use from 200–500 grams for the analysis, according to the purity of the lead; generally, 200 grams will be sufficient. Clean the lead, flatten it out to a thin plate of about 0.5 cm. thickness on a steel anvil, and cut into pieces about 2–3 cm. square. Place the weighed sample in a 2 liter flask, add 1275 cc. of water, and 325 cc. of nitric acid, Sp. Gr. 1.40. Dissolve by carefully warming on a water-bath or sand-bath. If the evolution of gas becomes too violent, remove the flask from the heat for a short time, without, however, cooling the liquid sufficiently to precipitate lead nitrate.

After about 3 hours, the solution will be complete, and the liquid will be perfectly clear, if the lead does not contain more than 0.02–0.03 per cent. of antimony. If lead antimonate has precipitated, filter, and wash the precipitate with water; the treatment of this precipitate will be given later. Now add 170 cc. of dilute sulphuric acid (1 part conc. acid : 2 parts water) to the nitric acid solution to precipitate the lead, and fill to the mark with distilled water. After shaking the contents sufficiently to thoroughly mix, allow the precipitate to settle, and siphon off the greater part of the clear supernatant liquid without disturbing the precipitate. The siphon should be filled with the solution in the flask. Evaporate 1750 cc. of the clear solution to dryness, and heat the residue until white fumes of sulphur trioxide are evolved; cool, dissolve in 50–60 cc. of water, and filter out the small amount of lead sulphate. As the latter may still contain a slight amount of antimony, dissolve it in hydrochloric acid, dilute with considerable water and saturate with hydrogen sulphide.

Separate the antimony sulphide from the lead sulphide by digestion with ammonium or sodium sulphide; the antimony may be reprecipitated as sulphide, by the addition of hydrochloric acid. Set the acidified solution aside temporarily. Pass a current of hydrogen sulphide through the filtrate from the lead sulphate, at first at a temperature of 70–80° C., continuing the passage of the gas until the liquid becomes cold. When the precipitate has completely settled, filter, and digest the precipitate with a solution of potassium or sodium sulphide. Filter out the insoluble sulphides and reprecipitate the arsenic and antimony with dilute hydrochloric acid. Unite this precipitate with the antimony sulphide from the ammonium sulphide solution, wash with water, and remove the admixed sulphur with carbon bisulphide. See page 247.

If a residue of lead antimonate* remains on dissolving the lead in nitric acid, dissolve it in hydrochloric acid and tartaric acid, and precipitate with hydrogen sulphide. Extract the antimony in the precipitate by digesting with sodium sulphide, and reprecipitate with hydrochloric acid. The antimony (and arsenic) sulphide obtained after removing the lead sulphide, may be filtered on the same filter with the sulphides from the ammonium sulphide solution.

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* This residue may also contain arsenic.

Dissolve the mixture of antimony and arsenic sulphides in pure potassium hydroxide, and proceed as given on page 89.

Arsenic and antimony may also be separated as follows: Add fuming nitric acid to the dried precipitate in a large porcelain crucible; when the paper fiber is completely destroyed and the greater part of the nitric acid is removed by evaporation, dilute with water, add sodium carbonate in slight excess, and a little sodium nitrate.

Evaporate to dryness, fuse, and continue the heating until the mass appears white. Cool, extract the mass with water, and wash the insoluble sodium antimonate, first with water and then with dilute alcohol. Dissolve the residue in hydrochloric acid and a little tartaric acid, and precipitate the antimony with hydrogen sulphide.

The filtrate from the sodium antimonate contains sodium arsenate together with a little antimony. Remove the alcohol by heating, acidify with dilute sulphuric acid, concentrate, to remove the nitric acid, and precipitate the arsenic and antimony with hydrogen sulphide, as given above. Filter, wash the precipitate, and treat on the filter with a cold, concentrated solution of ammonium carbonate, which dissolves the arsenous sulphide, while the antimony sulphide remains insoluble. Repeat the operation a few times with small quantities of solution, to remove all the arsenous sulphide. The arsenic may be reprecipitated as sulphide in the filtrate by acidifying with hydrochloric acid, adding a little hydrogen sulphide water, and warming to expel carbon dioxide. Filter on a paper dried at 110° C., dry the precipitate at the same temperature, and weigh.

Filter out the 2 antimony precipitates and wash. The filter tube described on page 15 may be used to collect the precipitate.

Dissolve the sulphides of copper, cadmium, etc., insoluble in potassium sulphide, in dilute nitric acid (1 :2), add dilute sulphuric acid, and evaporate to fumes of sulphuric anhydride. If a white residue of lead sulphate remains behind when the cooled mass is dissolved in water, filter, and wash it with water containing hydrogen sulphide.

To separate bismuth from the other metals, nearly neutralize the solution with sodium carbonate, add potassium cyanide, and warm gently on the water-bath. Filter out the potassium-bismuth cyanide, wash with water, dissolve in dilute nitric acid and precipitate the bismuth as carbonate. For this purpose add ammonium carbonate to the solution in slight excess, and heat for some time at the boiling point. Filter off the bismuth carbonate, wash and ignite. Weigh as Bi_2O_3.

Add a little more potassium cyanide to the filtrate from the potassium-bismuth cyanide to prevent the precipitation of copper, and add a few drops of potassium or sodium sulphide. Filter out the precipitate of silver sulphide and cadmium sulphide, wash with water and dissolve in dilute nitric acid. Precipitate the silver* with a few drops of hydrochloric acid, concentrate the filtrate and precipitate the cadmium as carbonate.

The copper is contained in the filtrate from the silver and cadmium sulphides. Acidify with sulphuric acid, heat until the odor of hydrocyanic acid has disappeared, and precipitate the copper with hydrogen sulphide.

The filtrate from the original sulphide precipitate contains iron, zinc, etc. Add ammonium hydroxide and ammonium sulphide, and filter out the sulphides. If a little nickel sulphide is dissolved, as is usually the case, it may be precipitated in the filtrate by adding dilute acetic acid.

On treating the sulphides on the filter with dilute hydrochloric acid and hydrogen sulphide water, iron, zinc and manganese sulphides are dissolved, while the sulphides of cobalt and nickel remain undissolved. Oxidize the solution with nitric acid, and separate iron and zinc by repeated precipitation of the former with ammonium hydroxide. Ignite the ferric hydroxide and weigh as Fe_2O_3.

Acidify the filtrate from the ferric hydroxide with acetic acid, and precipitate the zinc with hydrogen sulphide; after standing 24 hours, filter, and determine the zinc sulphide as such.

To determine the manganese, concentrate the filtrate from the zinc sulphide, add ammonium hydroxide and ammonium sulphide and allow to stand for 24 hours. Filter out the manganous sulphide and determine it as given on page 38.

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* The most accurate method of determining silver is by cupellation, as given on page 238 The silver may be determined gravimetrically in a special portion as follows: Dissolve 200 grams of lead in dilute nitric acid, dilute largely with water and precipitate with a few drops of hydrochloric acid. Allow the precipitate to settle, and filter. Ignite to metallic silver in a current of hydrogen.

Dissolve the sulphides of cobalt and nickel in hydrochloric acid containing a little nitric acid, evaporate nearly to dryness and add ammonium hydroxide to alkaline reaction. If a slight precipitate is formed, filter, and precipitate the cobalt and nickel in the filtrate by boiling with potassium hydroxide. Separate the cobalt and nickel as given in page 33.

In the calculations, the volume of the lead sulphate in the measuring flask must be considered. 100 grams of lead in the form of lead sulphate, occupy a volume of 23 cc.; 200 grams, 46 cc. In the calculation, therefore, the 1750 cc. are not to be referred to 2000 cc., but to 2000—46=1954 cc., or 179.12 grams of Refined Lead.

The above method is also applicable to 'Work Lead'. 10–50 grams of the lead will be sufficient. If the lead contains sulphur, determine it as given on page 181.

HARD LEAD.

As a rule, antimony is the only constituent determined in Hard Lead. For this determination, the method given on page 80, may be used. If a complete analysis is desired, the method given under Refined Lead may be used.

ANTIMONY*.

Metallic antimony may be analyzed by the method given under Refined Lead, or Hard Lead. If antimony is fused with sodium carbonate and sulphur and the fused mass extracted with water, the insoluble residue contains the sulphides of lead, cadmium, copper, bismuth, iron, nickel, manganese, and zinc. The solution contains antimony, arsenic and tin, which may be separated by the method given on page 90.

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* To determine antimony in antimony slags, proceed as given under Hard Lead.

Determine the sulphur by the method given on page 180, using hydrochloric acid and tartaric acid for the decomposition.

ZINC.

SPELTER.

Zinc contains from 0.5–2.0 per cent. of Lead, together with more or less Iron, Cadmium and Arsenic, and occasionally Antimony, Manganese, Copper, Tin and Sulphur.

Hang a piece of the zinc weighing 50–100 grams, by a platinum wire in a beaker 3/4 filled with dilute sulphuric acid, so that the zinc is about half immersed in the acid. After a sufficient quantity of the metal has dissolved, filter quickly through a folded filter and wash.

A solution of pure zinc sulphate may be obtained by this method, as no other metals will be dissolved as long as undissolved zinc is present. The metallic impurities contained in the zinc will be deposited on the surface of the zinc, or fall to the bottom of the beaker. Free the undissolved zinc from the spongy deposit, wash off with water, dry and weigh. The amount of zinc in solution is obtained by difference.

Digest the spongy mass and the residue on the filter with nitric acid, and evaporate to dryness. Add dilute nitric acid to the dish and warm until all the soluble matter is in solution ; tin, if present, will be in the form of stannic oxide, and the residue may also contain antimony oxide, silica and carbon. Filter, and wash the residue ; digest with sodium sulphide solution, filter, and treat the filtrate as given on page 88.

If the zinc contains silica and carbon, it is preferable to determine these constituents in a special sample, after solution in nitric acid, Evaporate to dryness, warm the residue with dilute hydrochloric acid, filter out the silica and carbon and wash with hot water. Determine the carbon by combustion in a current of oxygen (see : Organic Analysis), and weigh the residual silica. The silica should be tested for impurities.

Precipitate the metals in the hot filtrate from the stannic oxide, etc., with hydrogen sulphide and digest the sulphides with potassium sulphide. As a portion of the arsenic and antimony are evolved as arsine and stibine during solution of the zinc, these elements must be determined in a special sample. See below.

Filter out the sulphides insoluble in potassium sulphide, dissolve in dilute nitric acid, add sulphuric acid and concentrate until all the nitric acid is expelled. Add water and alcohol to the cooled mass, filter out the lead sulphate and wash it with dilute alcohol.

Heat the filtrate from the lead sulphate to expel the alcohol. Add ammonium hydroxide and ammonium carbonate, allow to stand for some time and filter out the cadmium carbonate. Dissolve the precipitate in hydrochloric acid and repeat the precipitation. Ignite to CdO.

Acidify the filtrate from the cadmium carbonate, with hydrochloric acid, and precipitate the copper with hydrogen sulphide.

The filtrate from the cuprous sulphide contains the metals of the ammonium sulphide group. Add ammonium hydroxide and ammonium sulphide; separate the sulphides according to the method given under Refined Lead.

Determination of Arsenic and Antimony:—Dissolve 20–50 grams of the zinc in aqua regia, evaporate the excess of acid and precipitate the metals with hydrogen sulphide. Separate the metals as given on page 89. If tin is present, it must be separated as given on page 90.

If the zinc evolves hydrogen sulphide when treated with sulphuric acid*, determine the sulphur by the method given on page 181.

If it is desired to determine the zinc alone, treat a weighed sample with acid in a suitable apparatus and calculate the amount of zinc from the volume of hydrogen. See page 185.

BLACK COPPER.†

Copper, Iron, Lead, Silver, Arsenic, Antimony, Bismuth, Zinc, Nickel, Cobalt and Sulphur.

Clean the surface of the copper with a chisel, and digest 500–100 grams of copper chips, according to the purity, in nitric acid, Sp. Gr. 1.20, until all soluble matter is in solution. Dilute with water, filter out the insoluble matter, wash with water, transfer to a 2 liter flask, and dilute to the mark.

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* Test by passing the gas into alkaline lead solution.

† The simplest method of analyzing Black Copper, is by electrolysis. See: Foot Note, p. 1. Fresenius has worked out a method (Zeit. f. anal. Chem., Vol. 21, p. 229), without the use of electrolysis, which is essentially the same as given above.

Heat the insoluble residue, consisting of tin, antimony, arsenic, and small amounts of copper, lead, etc., in a porcelain crucible with dehydrated sodium thiosulphate, extract the fuse with water and filter out the insoluble sulphides (copper, lead, etc.). The solution may contain arsenic, antimony and tin; separate them as given on page 90.

Digest the insoluble sulphides of copper, lead, etc., with nitric acid and a few drops of hydrochloric acid. If any silver chloride is precipitated, filter it out on a weighed filter, and evaporate the filtrate on the water-bath, after adding sulphuric acid. Determine the lead as sulphate, and precipitate the bismuth in the filtrate as oxychloride.

Divide the main solution into two portions of 1 liter each. To one portion, add a few drops of hydrochloric acid; if a precipitate is produced, proceed as given above.

Add 85 grams of concentrated sulphuric acid, with the necessary precautions, to the filtrate from the silver chloride, assuming that each liter contains 50 grams of copper, evaporate on the water-bath to expel the nitric acid, and then dilute with water.

Filter the solution, wash the residue of lead sulphate with dilute sulphuric acid and then with alcohol. As the alcoholic washings contain no metals in solution, they may be received in a separate beaker. Determine the lead sulphate as such, and test it for impurities*.

Dilute the filtrate from the lead sulphate to about 4 liters, add 200 cc. of hydrochloric acid, Sp. Gr. 1.12, warm the solution to 70–80° C., and pass hydrogen sulphide until the solution smells strongly of the gas.

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* It must be completely soluble in ammonium acetate.

Transfer the solution and precipitate to a tared 6 liter flask, and weigh. From the weight of the flask, solution and precipitate, the weight of the solution may be obtained by subtracting the weight of the empty flask and the weight of cuprous sulphide corresponding to the weight of copper contained in 1 liter of the solution.

When the precipitate has settled, siphon off as much of the clear solution as possible and weigh the flask + precipitate + the rest of the solution.

Evaporate the clear solution in a porcelain dish, and expel the greater part of the sulphuric acid by heating on a sand-bath ; cool, add water, oxidize the iron with hydrogen peroxide or nitric acid, and precipitate it with ammonium hydroxide. Filter out the precipitate of ferric hydroxide, wash with hot water, dissolve in hydrochloric acid, and reprecipitate. The filtrate contains nickel, cobalt and zinc, which may be separated as given above. The amounts of iron, nickel, etc., found, are to be calculated to the total amount of solution (2 liters).

The precipitate of cuprous sulphide contained in the flask still contains a small amount of arsenic, antimony and tin.

For their determination, add sodium or potassium hydroxide in slight excess to the contents of the flask, add a sufficient amount of sodium or potassium sulphide and warm on the water-bath. Cool the solution, rinse into a tared flask and weigh again ; after the copper sulphide has settled, siphon off the clear solution and weigh the flask and remainder of the solution. Add dilute sulphuric acid to the clear portion siphoned off, to precipitate the sulphides of arsenic, antimony and tin. Separate these elements as given on page 90. Calculate the amounts of arsenic, antimony and tin, to the total solution. Filter out the copper sulphide, wash with water containing a little sodium sulphide, dissolve in nitric acid containing a little hydrochloric acid and evaporate to expel the nitric acid. Repeat the evaporation with hydrochloric acid to ensure the complete removal of the nitric acid. Dissolve the salts in water and filter off the precipitate of bismuth oxychloride. As the latter contains a small amount of copper, dissolve it in hydrochloric acid, add potassium hydroxide to alkaline reaction, add potassium cyanide in excess and then add potassium sulphide. The precipitated bismuth sulphide may be determined as such, or transformed into bismuth oxide.

Determination of Sulphur :—Add barium nitrate to 400 cc. of the original nitric acid solution, and determine the barium sulphate as usual.

To determine phosphoric acid, evaporate 400 cc. of the original solution several times with hydrochloric acid to expel the nitric acid, transfer to a tared flask of about 2 liters capacity, and dilute to about 1500 cc. with water; warm the solution, saturate with hydrogen sulphide, and weigh.

Allow the precipitate to settle, siphon off a portion of the weighed solution, evaporate repeatedly with nitric acid and precipitate the phosphoric acid with ammonium molybdate.

REFINED COPPER.

Refined copper contains Cuprous Oxide, together with the Metals contained in Black Copper.

See the preceding example, for the determination of the elements contained in Black Copper.

The determination of cuprous oxide is based on its reaction with a dilute, neutral solution of silver nitrate; copper nitrate, basic copper nitrate and metallic silver being formed, the latter two being precipitated:

$$3Cu_2O+6AgNO_3+3H_2O=2Cu(NO_3)_2+2Cu_2(OH)_3NO_3+6Ag$$

Dissolve about 5.5 grams of silver nitrate in 100 cc. of water and add about 1 gram of the copper. After complete decomposition (in the cold), filter, wash the residue, and dissolve it in dilute nitric acid. Precipitate the silver with hydrochloric acid, and determine the copper in the filtrate. The copper found, multiplied by:

1.5, gives the amount of copper present as cuprous oxide;
1.68948, gives the amount of cuprous oxide;
0.18948, gives the amount of oxygen contained in the cuprous oxide. (Hampe.)

TIN.

The ordinary impurities are: Copper, Lead, Bismuth, Iron, Zinc, Arsenic and Antimony.

If metallic tin is dissolved in dilute nitric acid, stannic oxide remains insoluble when the excess of acid is evaporated.

The stannic oxide, however, always contains appreciable amounts of other metals, especially copper, lead and antimony. On fusing the washed residue with sodium carbonate and sulphur, or better, dehydrated sodium thiosulphate, and extracting the fuse with water, the copper and lead remain insoluble in the form of sulphides; the sulphides of arsenic, antimony and tin in solution, may be reprecipitated with hydrochloric acid, and determined as given on page 91.

The sulphides that are insoluble in sodium sulphide, are dissolved in nitric acid and added to the principal solution.

The method of analysis follows from what has been said in the preceding examples.

BISMUTH.

Contains: Lead. Silver, Copper, Arsenic, Iron, Cobalt, Nickel and Sulphur.

Dissolve a considerable quantity of the metal in dilute nitric acid, evaporate the excess of acid, and precipitate the small amount of silver with hydrochloric acid. Enough of the latter reagent must be added so that on diluting with water, bismuth oxychloride is not precipitated.

Filter out the silver chloride, and precipitate the bismuth in the filtrate as oxychloride. See pages 70 and 72. Separate the bismuth oxychloride from the copper by the method given under Black Copper.

The filtrate contains the remaining elements, which may be separated and determined by the methods previously given. See page 220.

SILVER.

Generally contains traces of Gold, Lead, Copper, Antimony and Arsenic.

To determine the gold, dissolve from 25–50 grams in chlorine-free nitric acid, and determine the gold as given under Galenite, page 239.

NICKEL.

CUBE NICKEL.

Contains: Copper, Arsenic, Antimony, Iron, Cobalt, Sulpnur, (Carbon), and Silica.

Compare: Analysis of Nickel Matte, page 219.

Carbon may be determined by the method given under Pig-Iron.

PIG-IRON, STEEL (CHROME-STEEL, TUNGSTEN-STEEL), SPIEGELEISEN, FERRO-MANGANESE, FERRO-SILICON.

The elements determined in a complete analysis are: Iron, Manganese, Copper, Zinc, Cobalt, Nickel, Chromium, Vanadium, Tungsten, Aluminum, Titanium, Antimony, Arsenic, Manganese,Calcium, Silicon, Phosphorus, Sulphur and Carbon. The Carbon is partly Combined (Carbide and Hardening Carbon) and partly in the form of Graphitic (and Temper) Carbon.

Among the metals, those most commonly determined are: Manganese, Copper, Nickel and Chromium. The determination of Silicon may be combined with their determination, as it is always separated in the form of silica.

Dissolve from 5–10 grams of the pulverized iron or turnings, in hydrochloric acid, Sp. Gr. 1.124, in a platinum or good porcelain dish, and evaporate to dryness on the water-bath. The amount taken for analysis should depend upon the amount of the constituent present. Moisten the residue with hydrochloric acid, dissolve in water and filter out the insoluble matter. The residue contains the silicon as silica, graphite, chromium and phosphides and carbides of iron. After drying, ignite the filter and insoluble matter in a platinum crucible, until nearly all the graphite has been burned off, and then fuse with 4–5 times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate; if the carbon has not been completely burned off, add a little more potassium nitrate.

Allow the fuse to cool, dissolve in water, filter, and wash the residue. Acidify the filtrate with hydrochloric acid, and evaporate to dryness and separate the silica. Proceed as given on page 187.

Dissolve the insoluble part of the fused mass in hydrochloric acid, evaporate to dryness, moisten the residue with hydrochloric acid, dissolve in water and add to the main solution. Dilute the latter to a definite volume, A, (500 cc.)

In the separation of silica with hydrochloric acid by the preceding method, it always contains iron, etc.; for this reason fusion is necessary. If it is desired to determine silica only, Drown and Shimer recommend to dissolve the iron in nitric acid of Sp. Gr. 1.2 (12 cc. acid to 1 gram of iron), in a porcelain or platinum dish, add concentrated sulphuric acid (1.5 cc. for each gram of iron) mix, and evaporate almost to dryness.

After cooling, add sufficient water to dissolve all the salts of iron, warm, filter and wash the residue with hot water, then with 25–30 cc. of hydrochloric acid, Sp. Gr. 1,112, and finally with hot water. Ignite and weigh the silica.

V. Jueptner recommends dissolving the borings in a porcelain dish in concentrated hydrochloric acid with a small amount of potassium chlorate. After solution, evaporate to dryness on the water-bath ; cool, moisten with concentrated hydrochloric acid, allow to stand a short time, and then dilute with water. Filter out the insoluble silica, wash first with dilute hydrochloric acid (1–1), and then with water. Ignite and weigh as SiO_2.

Ferro-silicon, which is high in silicon and is decomposable neither by hydrochloric acid nor nitric acid, should be fused direct with 5–6 times its weight of potassium-sodium carbonate. Separate the silica from the aqueous solution of the fuse, as given above.

For the purpose of a check in works, where absolute accuracy is not required, the following rapid method may be used for determining silicon in pig-iron. Fuse about 1 gram of the borings direct with 25 grams of potassium bisulphate in a large platinum crucible, cool, and dissolve in hot hydrochloric acid and water. Filter, and wash the silica with hydrochloric acid and water. When the silicon is from .5–3.5%, the method gives sufficiently accurate results and a determination can be made in 1 1/2 hours.

A number of the foreign metals may be determined in solution A, page 272, in case it is not preferred to determine the individual elements in special samples.

Determination of Manganese, Nickel and Cobalt :—A measured portion, e. g. 250 cc., of solution A is warmed, and the metals of the hydrogen sulphide group (copper, arsenic, antimony) precipitated by that reagent. After the precipitate has been washed, it may be rejected, as it is preferable to determine these elements in special samples.

After expelling the hydrogen sulphide, oxidize the iron with nitric acid, hydrogen peroxide or bromine, and test for complete oxidation with potassium ferricyanide. Dilute the solution, transfer to an Erlenmeyer flask, carefully neutralize with a solution of sodium carbonate, add a few drops of acetic acid, and sodium acetate (about 6 grams to 1 gram iron) and boil. The precipitate of basic ferric acetate also contains the total phosphoric acid, all of the titanic acid, the alumina, and small amounts of cobalt, nickel and manganese. Filter on 2 large filter papers, wash a few times with boiling water, dissolve in hydrochloric acid and repeat the precipitation. If much manganese is present, the precipitation must be repeated several times or until the filtrate is not precipitated by bromine in potassium bromide* after neutralization with potassium hydroxide.

The separation of manganese, nickel and cobalt can be made in the filtrate, according to the method given on page 136.

Bromine may also be added to the alkaline solution. Warm on the water-bath until the black precipitate, consisting of the higher oxides of the 3 metals and a little ferric hydroxide, has settled. After expelling the bromine and reducing with alcohol any permanganate that may have been formed, filter out the precipitate and wash it with hot water. Dissolve the precipitate in hydrochloric acid and hydrogen peroxide, neutralize the solution, and separate the iron as basic acetate. To separate the nickel and cobalt from the manganese, add 20 cc. of acetic acid to the filtrate, transfer to a pressure flask† and treat with hydrogen sulphide, which precipitates the sulphides of

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[*] 60 grams potassium bromide, 700 cc. water, and 40 grams of bromine.

[†] Precipitation in a pressure flask is executed as follows: Saturate the solution with hydrogen sulphide, transfer to a thick walled flask of about 1 liter capacity (an ordinary suction flask used for filtering under

nickel and cobalt. Filter, and ignite the precipitate, incinerating the filter paper separately, and weigh as cobalt oxide and nickelous oxide. If it is desired to separate the cobalt, dissolve the weighed precipitate and separate the metals as given on page 33.

Instead of weighing the ignited oxides of nickel and cobalt, they may be transformed into sulphates, and the metals determined together by electrolysis.

Precipitate the manganese in the filtrate from the nickel and cobalt with ammonium sulphide.

The separation of large quantities of iron is greatly facilitated by Rothe's Method. This method is based upon the easy solubility of ferric chloride in ether containing hydrochloric acid, as well as the insolubility or difficult solubility of the chlorides of copper, manganese, nickel, cobalt, aluminum, chromium and titanium, under these conditions.

The method, in general, is as follows: Add hydrochloric acid to the solution, and shake with ether in an apparatus which permits the separation of the ethereal layer containing the ferric chloride, and the layer containing the other chlorides. Since one of the essential conditions for a good separation of the two layers, is the complete absence of suspended matter, the latter, which may consist of silica, carbon, etc., must be removed.

To analyze an iron or steel by this method, dissolve 5

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diminished pressure, may be used). Mix the solution with an equal volume of saturated hydrogen sulphide water, fasten the stopper securely, and close the side tube (if a suction flask is used) with a piece of rubber tubing and a bit of glass rod. Support the flask in the water-bath by means of a stand so that the flask is immersed up to the neck and does not touch the bottom. Gradually heat the water to boiling and keep at this temperature for 3 hours. Allow the flask to cool in the water-bath. It is best to do work with pressure flasks, etc., in a special room.

grams of the sample in a platinum dish in 40 cc. of warm hydrochloric acid, Sp. Gr. 1.124. Evaporate to dryness and heat in the air-bath at 120° C. Add 20 cc. of hydrochloric acid, heat to boiling and filter out the silica after diluting with 3 times the volume of water. Wash the silica with hot water, dry, ignite and weigh. If, however,

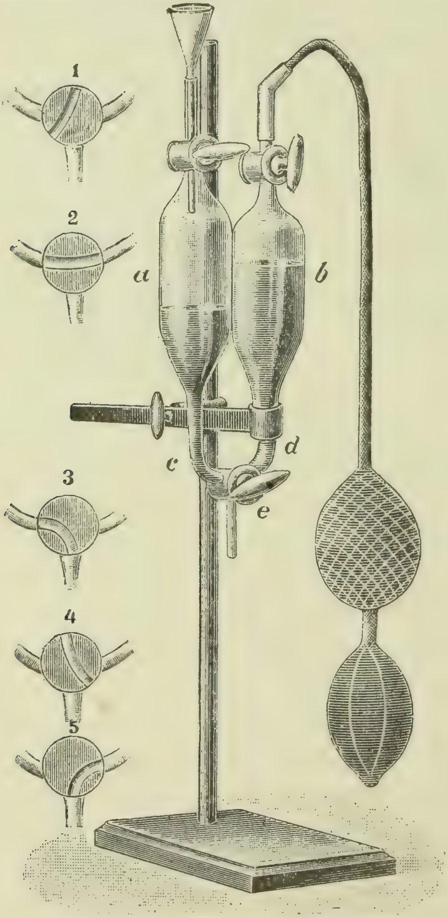

Fig. 42.

it is not desired to determine the silica, and the sample contains no graphite, hydrofluoric acid may be added to the solution before evaporation, to volatilize the silica as silicon tetrafluoride.

Dissolve the dry salts in hydrochloric acid, or use the filtrate from the silica, concentrate in a porcelain dish to remove the excess of acid and oxidize the solution with 2.–2.5 cc. of nitric acid, Sp. Gr. 1.40, adding the acid drop by drop.

Evaporate the solution to the consistency of syrup, or until ferric chloride crystallizes out, to expel free chlorine and nitric acid, which decomposes the ether. The solution, which should have a total volume of about 10 cc., is now ready for the separation.

The apparatus in which the separation is effected, is shown in Fig. 42. It consists or 2 pipette-shaped tubes, a and b, each of about 200 cc. capacity, communicating by the tube c d, about 2–3 mm. in diameter. The 3-way stop-cock e, allows the two sides of the apparatus to be connected by the position shown in 2; the positions 1 and 4 disconnect the two sides, and the positions 3 and 5 allow either side to be emptied. The upper ends of the 2 sides are provided with simple stop-cocks.

Disconnect the two sides of the apparatus, transfer the solution to the side a, by means of a long stemmed funnel, and rinse the dish and funnel with sufficient hydrochloric acid of the above strength to make the total volume about 55–60 cc. Now add 100 cc. of ether to the side b, and produce a slight excess of pressure over the ether by means of the rubber bulb. On connecting the two sides of the apparatus with the lower stop-cock in position 2, the ether is forced up through the iron solution. The apparatus must be cooled in a stream of water, as considerable heat will be generated. As soon as about 9/10 of the ether has been forced over, disconnect the two sides of the apparatus with the lower stop-cock, and close the upper stop-cocks.

Shake the contents of the flask for a short time while cooling in the stream of water, and then transfer the remainder of the ether over into a. The last reserve portion of ether serves to rinse from the capillary tube c, any iron solution which has not come in contact with the first portion of ether. Now close the apparatus above and below, shake again and allow to stand quiet for 2–3 minutes ; this allows a separation of the green colored ethereal layer above, containing the iron, and the hydrochloric acid solution below, containing the foreign metals, which, however, is generally covered more or less by ferric chloride.

Open the stop-cock e and allow the heavy lower layer to flow over into the side b, leaving just enough in the side a, to fill the capillary tube c. Disconnect the two sides again, and shake the apparatus, to rinse any adhering acid solution from the sides of the flask, and allow to stand quiet for a few minutes. When the ethereal layer is perfectly clear, transfer the remainder of the heavy layer to b, and do not close the lower stop-cock until a little of the ethereal layer has passed over into d.

Draw off the ethereal layer containing the iron into a beaker. Close the 3-way stop-cock and rinse the walls of the side a with a small amount of ether. When the washings have collected in c, it can readily be seen whether any foreign metals are still present. If such is the case, transfer the lower layer containing them to the side b. Finally rinse the side with a little ether and add to the iron solution.

A single shaking with ether never suffices to remove all the iron. Therefore add 50 cc. of ether in a, and repeat the operation. It is generally necessary to repeat the shaking 2–3 times to remove all the iron.

Add hydrochloric acid to the solution containing the foreign metals and a little ether, heat on the water-bath to volatilize the ether, and finally evaporate to dryness. Separate the metals as given on page 268.

The method to be used if aluminum is present, is given below. Titanium and chromium must be separated according to the usual methods; their determination should be made in a special sample. See below.

As copper and cobalt chlorides are slightly soluble in ether, if large quantities of these metals are contained in the sample, (which, however; is not the case with iron and steel), it is necessary to shake the first and second ethereal iron solution with 10 cc. of hydrochloric acid, Sp. Gr. 1.104, and draw off the lower layer containing the copper and cobalt, into a separate beaker.

Determination of Aluminum:—Aluminum is never contained in iron unless intentionally added. Dissolve 6 grams of the metal and prepare the solution for extraction with ether exactly as given in the preceding method. The final hydrochloric acid solution obtained by concentration should contain no precipitate of basic aluminum salts, and should be perfectly clear.

Free the solution from iron by shaking twice with ether, and evaporate the iron-free solution to dryness on the water-bath. Dissolve the salts in hydrochloric acid and water, add about 6 grams of sodium acetate to the solution, heat to boiling and precipitate the aluminum by adding 2 cc. of a concentrated solution of sodium phosphate. Filter out the aluminum phosphate, and wash with hot water. The precipitate is generally contaminated with traces of iron, manganese and copper. Dissolve in hydrochloric acid in a platinum dish, evaporate to dryness, add 2–3 cc. of water and 2 grams of sodium hydroxide that contains no aluminum. Boil for some time, transfer to a 300 cc. graduated flask, and dilute to the mark. Filter off 250 cc., acidify with acetic acid, boil, and precipitate the aluminum as phosphate.

In the case of iron containing but little manganese, the first precipitation with sodium phosphate may be omitted, by evaporating the solution to dryness and treating at once with 5 cc. of water and 5 cc. of sodium hydroxide.

Determination of Manganese :—In many cases, a determination of manganese, without regard to the other constituents, is desired. A convenient method is the one devised by Volhard, which is applicable in the analysis of ferro-manganese and all irons and steels.

Dissolve a weighed sample in warm hydrochloric acid Sp. Gr. 1.124, in a calibrated liter flask. The quantity to be taken depends upon the nature of the substance ; for ferromanganese use .5 gram sample and 30 cc. of acid, and for spiegeleisen, white pig-iron and other irons, 2.5 grams and 50 cc. of acid. When the sample is in solution, cool, dilute with 50–100 cc. of water, oxidize the iron with 2–3 grams of potassium chlorate, boil off the chlorine and test for ferrous iron with potassium ferricyanide.

Dilute to the mark, and draw off 200 cc. of the solution for titration. Transfer to an Erlenmeyer flask of 1 liter capacity, dilute with 200 cc. of water, warm to at least 50° C., and add zinc oxide suspended in water, until the solution appears milky. An unnecessary excess of zinc oxide should be avoided. Heat the solution to boiling, and titrate with permanganate solution, without filtration, until the pink color of permanganic acid is permanent after standing for some time.

The presence of free zinc oxide renders the titration possible even if the manganese is present as manganous chloride, as the free hydrochloric acid liberated during the reaction, which would hinder the formation of manganese dioxide, is neutralized by the excess of zinc oxide :

$$3MnCl_2 + 2KMnO_4 + 2H_2O = 2KCl + 5MnO_2 + 4HCl$$

$$4HCl + 2ZnO = 2ZnCl_2 + 2H_2O.$$

Another method for the volumetric determination of manganese, has been suggested by Hampe. The method is based upon the oxidation of the manganese to manganese dioxide by potassium chlorate and boiling nitric acid. The manganese dioxide formed is reduced by an excess of standard ferrous iron solution, and the excess of the latter titrated back with permanganate.

The following reactions take place :

$$KClO_3 + HNO_3 = HClO_3 + KNO_3\,;$$

$$2HClO_3 + Mn(NO_3)_2 = \underbrace{MnO_2}_{\text{insoluble}} + 2ClO_2 + 2HNO_3\,;$$

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O,$$

Nitric acid, Sp. Gr. 1.42, and successive additions of potassium chlorate, are necessary to precipitate pure manganese dioxide.

This method is especially suitable for irons low in silicon (ferro-manganese, spiegeleisen, etc.), as high silicon irons require previous filtration to remove the silica.

The method is as follows: Dissolve from 1–10 grams, according to the amount of manganese, in 20–50 cc. of nitric acid* in an Erlenmeyer flask, add potassium chlorate in small portions, and boil for 5–10 minutes. Cool, dilute with water, filter out the manganese dioxide and wash with water. Pierce the point of the filter paper and rinse the precipitate back into the flask. Drop a few cc. of the standard ferrous sulphate solution onto the filter from a burette and rinse into a flask, add a sufficient amount of the ferrous sulphate solution to reduce the manganese dioxide, close the flask with a 'Bunsen valve' and warm on the water-bath to complete solution. Titrate back the excess of ferrous iron with permanganate. See: Volumetric Analysis.

[Julien,† has recommended a modification of the above method which considerably shortens the process without sacrificing accuracy. Obtain the manganese dioxide exactly as given above; when the manganese is all oxidized to dioxide, cool, and dilute to 400–450 cc. Now add from a burette an excess of standard hydrogen peroxide, to completely dissolve the precipitate. Titrate the excess of hydrogen peroxide with potassium permanganate. The method is suitable for all compounds of iron and manganese, and has come into extensive use in American steel works.]

For spiegeleisen high in manganese and for ferromanganese, use a solution of ferrous-ammonium sulphate containing 71.4085 grams per liter; before diluting to the mark, add 50 cc. of sulphuric acid. 1 cc. of this solution corresponds to 0.005 gram of manganese. A corresponding permanganate solution is obtained by dissolving 5.7547 grams of pure, crystallized potassium permanganate in 1 liter of distilled water. It is advisable to standardize the permanganate solution independent of the ferrous-ammonium sulphate solution, and then to check the latter against the former.

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* In the case of irons containing graphite, in which the method is not so suitable, use 3-4 times as much nitric acid as is given above.

† [Jour. Brit. Iron and Steel Inst., 1898–II, p. 557].

Oxalic acid, as well as ferrous sulphate, may be used in standardizing the permanganate solution. See : Volumetric Analysis, Potassium Permanganate and Ferrous Salts.

If the solution being titrated contains a large excess of sulphuric acid, it hinders the formation of manganese dioxide by nitric acid and potassium chlorate. To remove the sulphuric acid, add barium nitrate. The small amount of sulphur usually contained in irons, however, need not be considered in this respect. Large amounts of cobalt, lead and bismuth interfere with the determination of manganese. In this case also, good results may be obtained by dissolving the precipitate in a mixture of nitric acid and oxalic acid and repeating the oxidation with potassium chlorate. Copper, zinc, nickel and tin do not interfere, so that the method is suitable for the determination of manganese in commercial metals and alloys.

Gravimetric Determination of Manganese :—First separate the iron by the basic acetate method or by extraction of the ferric chloride with ether. The manganese may then be precipitated as sulphide. It should be remembered, however, that cobalt, nickel, zinc, etc., are also precipitated ; their separation is given on page 274. Manganese may also be precipitated in the filtrate from the basic ferric acetate, by oxidation with bromine. Add ammonium chloride and ammonium hydroxide, and then pass air saturated with bromine vapor through the solution. Filter out the precipitate, wash, ignite to Mn_3O_4, and weigh.

Determination of Tungsten :—Tungsten is rarely contained in ordinary iron, but is contained in tungsten steel in considerable quantity. In analysis, it is oxidized to tungstic acid ; either aqua regia or bromine is used for this purpose. In the first case, add aqua regia to the turnings, warm to solution and finally evaporate to dryness. In the case of bromine, which has the advantage that but little tungstic acid separates at first and that the iron dissolves more quickly, pour water on the filings and then add the bromine in successive small portions. In both cases, the final solution must be in nitric acid. Evaporate to dryness repeatedly with nitric acid, then dissolve the salts in nitric acid and filter off the tungstic (and silicic) acid. As the tungstic acid still contains iron, fuse it in a platinum crucible with sodium carbonate, extract with water and filter out the ferric oxide.

Transfer the filtrate containing the sodium tungstate to a porcelain dish, acidify with nitric acid, and evaporate to dryness on the water-bath. Digest the residue with dilute nitric acid, filter, wash, ignite and weigh as $SiO_2 + WoO_3$. To separate the silica from the tungstic acid, fuse them with 5 times their weight of potassium acid sulphate and continue the heating until no more particles of tungstic acid are visible in the mass. Cool, and extract the mass with a dilute solution of ammonium carbonate. Filter out the residual silica, wash with hot water, ignite and weigh.

Ziegler has suggested a simple method for the determination of tungsten. Dissolve the sample in nitric acid, Sp. Gr. 1.18, (16 cc. for each gram of iron); after solution, add twice the volume of dilute sulphuric acid (1 :5) and warm until the nitric acid has been expelled.

Dilute the solution with water, filter, wash with dilute hydrochloric acid and weigh the residue consisting of tungstic acid and silica (if the iron contained silicon). Then volatilize the silica by heating with a few drops of hydrofluoric acid, and ignite again; the residue is WoO_3.

Any residue insoluble in acid should be decomposed by fusion with potassium-sodium carbonate, and the silica then separated as given under Analysis of Silicates. Dilute hydrochloric acid should always be used for washing tungstic acid, as pure water causes the precipitate to pass through the filter.

Determination of Chromium and Vanadium:—Vanadium is often found in pig-iron, as it is a constituent of some Limonites. Chromium almost always accompanies vanadium, and is also intentionally added to iron in the manufacture of chrome steel. Chromium is found in but small amounts in pig-iron, but chrome steel and ferro-chrome contain considerable quantities.

The determination of chromium depends upon the formation of chromic acid, reduction of the latter by a measured excess of standard ferrous sulphate, and titration of the excess of the latter with potassium permanganate.

Dissolve 5–10 grams of pig-iron or steel in 5 times the amount of dilute hydrochloric acid (1. acid, Sp. Gr. 1.12 : 2. water), in absence of air to avoid oxidation if the iron, boil, and add twice the volume of water. Cool the solution, shake, and add a slight excess of barium carbonate;

now fill the flask with water, stopper, and allow to stand at the ordinary temperature for 24 hours, stirring occasionally.

The precipitate contains all of the chromium. Filter, wash quickly with cold water, ignite to burn off the graphite, and ignite for 2 hours with 10 times its weight of a mixture consisting of 4 parts of sodium-potassium carbonate and 6 parts of magnesia.

Alloys of iron and chromium, (ferro-chrome) which are not completely soluble in acids, may be decomposed by finely pulverizing, and igniting 2 grams with 1.25 grams of the carbonate mixture and 2 grams of magnesia, as given above.

Digest the sintered mass with hot water, which dissolves the alkaline chromate. Add dilute sulphuric acid and boil. After cooling, add a measured volume of ferrous sulphate,* and titrate back the excess with potassium permanganate; the end reaction is the change of color from green to violet. Titrate the same amount of ferrous sulphate with permanganate, and calculate the amount of chromium from the difference.

The end reaction on titrating chromium solutions with permanganate is not very sharp. Therefore, in determining small amounts of chromium in pig-iron, the gravimetric method is preferable. Add hydrochloric acid to the chromate solution and evaporate to dryness. Dissolve the salts in dilute hydrochloric acid, filter out the silica, add sodium carbonate and bromine-water and warm to oxidize the chromium to chromate. The chromate may be determined by the method given on page 208.

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* 50 grams of ferrous sulphate, 750 cc. of water, and 250 cc. of concentrated sulphuric acid.

The above method provides only for the determination of chromium. If it is desired to determine vanadium also, the precipitate produced by barium carbonate in the solution of a sample of steel or pig-iron, should be fused with 10 parts of sodium-potassium carbonate and 1 part of potassium nitrate. The water solution of the fuse contains the chromium in the form of chromate, and the vanadium as vanadate.

Add hydrochloric acid and alcohol, and evaporate to dryness. Dissolve in hydrochloric acid and water, filter out the silica, boil, and precipitate with ammonium hydroxide. To free the chromic hydroxide from phosphoric acid, dry the precipitate, ignite with the above mixture of sodium-potassium carbonate and magnesia, and extract with water; determine the chromium in the filtrate.

The filtrate from the chromium hydroxide contains the vanadium. Add yellow ammonium sulphide, which produce a red color in the solution. After neutralization, or slightly acidifying with acetic acid, allow to stand 24 hours, filter, and wash the vanadium sulphide with hydrogen sulphide water, ignite in an inclined crucible and weigh as V_2O_5.

Vanadium may be determined in ferro-chrome by the same method, by decomposing with alkaline carbonate and magnesia.

Separate Determination of Copper:—As this metal is contained in the pig-iron or steel in small proportions, 5–10 grams are necessary for the determination. If the sulphur has been determined by the method given on pages 292 and 181, the ferrous solution may be used for the determination of copper. Otherwise, dissolve the requisite quantity of metal in hydrochloric acid and saturate the solution with hydrogen sulphide and filter. Treat the sulphide precipitate with sodium sulphide to remove arsenic and antimony, dissolve the cuprous sulphide in nitric acid and precipitate the copper by electrolysis.*

Iron is generally calculated by difference. To determine it directly, dissolve a sample in hydrochloric acid, and titrate with either permanganate or stannous chloride.

In the former case, it is advisable to concentrate the solution by evaporation, to expel the absorbed carbon dioxide, as the latter may react with permanganate. It is self-evident that the solution must be reduced with zinc before titration. See Siderite.

Determination of Arsenic and Antimony :—Dissolve about 10 grams of pig-iron in aqua regia in a large beaker ; when no more action is visible, evaporate to dryness on the water-bath. Warm the salts with dilute hydrochloric acid, filter, and fuse the residue that was insoluble in aqua regia, with sodium carbonate and potassium nitrate. Dissolve the fused mass in water and add to the main solution. Reduce the iron to the ferrous condition by warming with sulphur dioxide or potassium bisulphite, and saturate the warm solution with hydrogen sulphide. Digest the sulphides with sodium sulphide, which dissolves the sulphides of arsenic and antimony. The latter may be separated and determined as given on pages 89 and 142.

This very exact method may be replaced by a more simple one. Dissolve 25–50 grams of the metal in hydrochloric acid, as given in the determination of copper. But slight traces of arsenic are evolved in the form of arsine, as iron behaves differently than zinc, and most of the arsenic is precipitated as such. Saturate the unfiltered solution with hydrogen sulphide, filter, wash the precipitate with hydrogen sulphide water and dissolve it in hydrochloric acid and potassium chlorate, after the free chlorine has been expelled by heat, which, in the presence of potassium chloride, can be accomplished without fear of loss; transfer the residue to the apparatus shown on page 91 and distil the arsenic. The residue in the distilling flask can be used for the determination of copper and antimony.

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* See: Foot Note, p. 1.

If several successive determinations of arsenic have to be made, v. Reis has suggested the following rapid method, which gives accurate and closely agreeing results. Dissolve 10–25 grams, according to the content of arsenic, in a large beaker, with 100 cc. of water and 20 cc. of concentrated sulphuric acid. When the action is over, boil for 10 minutes, filter and wash the residue. The latter contains the carbon and undissolved iron compounds, together with all of the metals of the hydrogen sulphide group. Transfer the residue to a beaker, add 20 cc. of water, 3–4 grams of potassium chlorate and 20 cc. of concentrated hydrochloric acid. Heat until all soluble matter is dissolved and the chlorine is expelled. Dilute with 25 cc. of water, filter and wash the residue with hot dilute hydrochloric acid. The solution contains all of the arsenic, and some copper and iron. V. Reis used ammonium sulpho-carbonate to separate arsenic from the remaining metals. If the arsenic solution contains a large quantity of iron (e. g. in pig-iron,) it is desirable to reduce the iron before precipitating with ammonium sulpho-carbonate. A convenient method for the reduction is to boil and add solid sodium hypophosphite in small portions. If but a small amount of iron is present, the ammonium sulpho-carbonate itself will serve as the reducer. Cool the solution, add a solution of the above reagent and stir vigorously for some time to collect the precipitate. When the precipitate has settled, filter, wash first with warm dilute hydrochloric acid, and then with hot water. Dissolve the precipitate off the filter with about 10 cc. of concentrated ammonium hydroxide.

Wash the filter with dilute ammonium hydroxide, and oxidize the warm filtrate and washings with about 10 cc. of hydrogen peroxide (containing no phosphoric acid). After cooling, precipitate the arsenic acid with magnesium chloride solution and determine as pyroarsenate. It is recommended to dissolve the precipitate in nitric acid, evaporate in a porcelain crucible and re-ignite. See page 96.

Ammonium sulpho-carbonate is prepared as follows: Shake together 500 cc. concentrated ammonium hydroxide and 50 cc. carbon bisulphide. To facilitate the combination, which is slow when aqueous ammonium hydroxide is used, it is desirable to use an alcoholic ammonia solution. Dilute the red-colored solution obtained with 4 parts of water. As the solution of the salt is strongly alkaline, care must be taken that the solution is acid after the precipitation; if necessary, add hydrochloric acid.

Determination of Titanium:*—For this determination, a large sample of iron must be taken; about 20–25 grams will be sufficient. Dissolve the iron in nitric acid, Sp. Gr. 1.18, evaporate to dryness in a porcelain dish, dissolve in hydrochloric acid, evaporate to dryness again and dissolve the residue in dilute hydrochloric acid. Filter out the insoluble matter, which consists of graphite and silica, as well as a small amount of iron. Evaporate the filtrate containing all the titanium and the rest of the iron, to about 50 cc., shake 2 times with 10 cc. of ether, as given on page 275. The titanium is contained in the chloride solution of the foreign metals, and partly separates out in a flocculent condition. Evaporate to dryness, treat the dry salts with hydrochloric acid and water, filter, wash and ignite the titanic acid.

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* [Compare Determination of Titanium in Magnetite.]

Titanium is precipitated with iron, aluminum and phosphoric acid, in the basic acetate separation.

In exact analysis, it is advisable to test for titanium in the filtrate from the basic acetate precipitate. Fuse the final precipitate with potassium bisulphate after washing with hot water, extract the fuse with water, filter out any silica that may be present, and precipitate the titanium in the filtrate by the method given on page 173.

Drown and Shimer determine titanium by first heating the iron in a porcelain boat in a current of dry chlorine. The chlorides of iron and manganese are condensed in greater part in the combustion tube, especially if the tube is somewhat longer than is ordinarily used. The chlorides of titanium and silicon may be absorbed in an apparatus partly filled with water. On subsequent boiling, the titanium and silica are precipitated. To obtain a quantitative separation, acidify the solution strongly with hydrochloric acid, add about 15 cc. of dilute sulphuric acid and evaporate until all the hydrochloric acid is expelled. Filter out the silica and precipitate the titanium by boiling the diluted filtrate, replacing the water as it evaporates.

Determination of Sulphur:—Sulphur may be determined by the method described on page 180, using about 10–15 grams of substance. If bromine is used, it reacts with the evolved hydrocarbons, forming oily drops of reddish yellow propylene bromide,* which separate out in the absorption tube; they disappear when the liquid is subsequently evaporated.

Fresenius determines the sulphur by treating the drillings with hydrochloric acid and passing the evolved hydrogen sulphide and hydrocarbons into an alkaline lead solution.

The apparatus used is shown in Fig. 43.

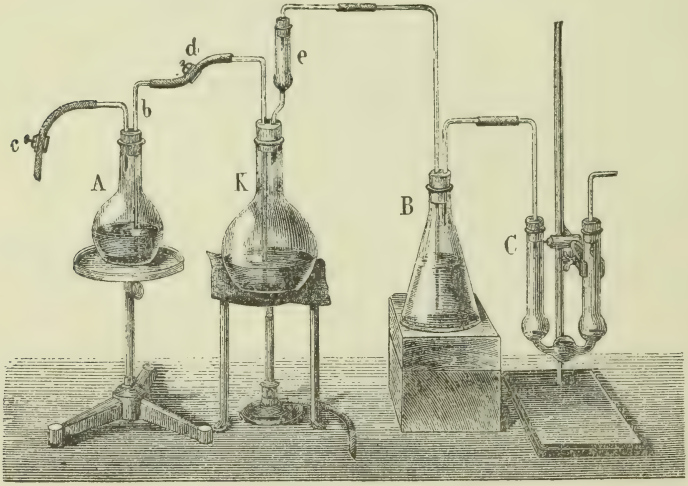

Fig. 43.

Place the weighed sample of iron in the flask K, and cover with water. The flask A contains the hydrochloric acid, Sp. Gr. 1.12 to be used for dissolving the iron, and B and C contain a solution of lead oxide in potassium hydroxide. Draw up the tube b until it is above the acid, open the stop-cock c, and fill the entire apparatus with purified hydrogen.

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* Cloez. Ber. deutsch. chem. Gesell. Vol. 7, p. 823.

Purify the hydrogen from hydrogen sulphide by passing the gas through a wash-bottle containing a solution of mercuric chloride. When the apparatus is filled with hydrogen, lower the tube b into the acid and again open the stop-cock c, which allows a quantity of acid to pass over into K; close the pinch-cock d, and warm the flask K until the iron is in solution. If there is not sufficient acid in the flask for complete solution, allow more to pass over. When the iron is all dissolved, draw the tube b out of the acid, pass a current of hydrogen through the apparatus, and heat the solution in K to boiling.

Filter out the lead sulphide in B and C., dry it, and fuse with sodium carbonate and potassium nitrate. The water solution of the fuse contains the sulphuric acid. To remove the small amount of lead which has passed into solution, pass a current of carbon dioxide, acidify with hydrochloric acid and evaporate to dryness. Dissolve the residue in dilute hydrochloric acid and precipitate the sulphuric acid with barium chloride.

In the case of certain difficultly soluble irons, it is possible that the solution in B might become acid, owing to part of the solution distilling over, and a portion of the lead sulphide be dissolved. It is desirable, therefore, to attach to the flask K, the condenser devised by the author. See page 58.

It has been ascertained by numerous experiments, that the hydrogen sulphide method is not applicable to all irons, as some contain sulphur that is not evolved by this method. In this case, filter, and wash the residue, rinse into a porcelain dish with hydrochloric acid, warm and gradually add potassium chlorate. Evaporate to dryness, dissolve in hydrochloric acid, filter, and precipitate the sulphuric acid in the filtrate. In the case of ferro-silicon, and pig-irons high in silicon, it is advisable to examine the hydrochloric acid solution for sulphur.

When iron is dissolved in dilute hydrochloric acid, all the sulphur present is not evolved in the form of hydrogen sulphide. A part is evolved as an organic compound, methyl sulphide, $(CH_3)_2S$, whose sulphur is neither oxidized to sulphuric acid, nor precipitated as metallic sulphide, and is, therefore, lost in the analysis. Although it is disputed by some chemists that there is a loss of sulphur in this manner—the amount of the organic compound is variable in different kinds of iron—it is advisable in exact analysis to pass the gas through an ignited tube by means of which the sulphur of the organic compound is changed to hydrogen sulphide.

A very convenient gravimetric method for sulphur has been recommended by Schulte. It consists in passing the hydrogen sulphide into a solution of cadmium acetate, transforming the precipitated cadmium sulphide into copper sulphide by means of copper sulphate and then igniting the copper sulphide to copper oxide. From the weight of the copper oxide, the weight of sulphur may be calculated.

It is not permissible to pass the gas into a solution of copper sulphate directly, as during solution, phosphine is evolved and the latter precipitates a compound of copper.

The details of the method are as follows: Transfer about 10 grams of the iron to the flask a, Fig. 44, by means of a wide funnel, and stopper with the condenser. The wash-bottles, b and d, contain a solution of cadmium acetate containing 25 grams of the salt in 200 cc. of concentrated acetic acid.

The tube c, of hard glass, should have a diameter of about 1 cm. and a length of about 35–40 cm. While filling the apparatus with carbon dioxide, heat the tube to a dull red. After all the air has been replaced by carbon dioxide, stop the current of the latter, and add a mixture of 100 parts hydrochloric acid, Sp. Gr. 1.24, and 100 parts of water, through a side tube, being careful to admit no air. Allow a small amount of acid to remain above the stopper for a seal.

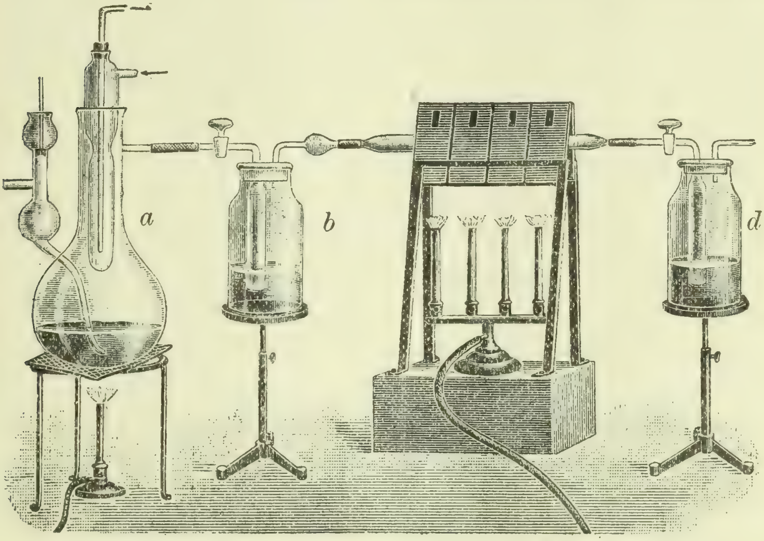

Fig. 44.

When the evolution of hydrogen noticeably slackens, light the flame under a. Gradually heat the contents of the flask to boiling, at the same time passing a current of cold water through the condenser. When no bubbles pass through the absorption bottles, pass a slow current of carbon dioxide through the apparatus, while the solution boils.

From time to time, test the gas through the 3-way stop-cock of the wash-bottle b, to see if it still contains hydrogen sulphide. When the latter is all driven over into the absorption flasks, extinguish the flame, rinse the contents of the absorption flasks into a beaker, and at once add 5–7 cc. of a copper solution containing 120 grams of copper sulphate in 800 cc. of water and 120 cc. of concentrated sulphuric acid. Shake the solution and then filter the copper sulphide on a small filter and wash with warm water until the filtrate is not precipitated by hydrogen sulphide. Press the filter paper together, place it in a weighed platinum crucible, incline on the triangle and heat gently until the paper is carbonized. Burn off the carbon, and then heat at the full heat of the burner for about a minute, to decompose any copper sulphate that might be formed. The weight of copper oxide multiplied by 0.4041 gives the equivalent amount of sulphur.

Gintl recommends the following methods for the determination of sulphur in pig-iron: Digest the finely divided iron with 20 times the quantity of a tolerably concentrated, neutral solution of ferric chloride, for 8–10 hours at a temperature of 25–30° C. Almost all the iron passes into solution in the form of ferrous chloride, and the residue contains the graphite, phosphide of iron and a little undecomposed iron, together with all the sulphur. Filter, wash, and fuse the residue in a silver crucible with a mixture of 3 parts potassium nitrate and 1 part potassium hydroxide. Digest the fused mass in water, filter, and precipitate the sulphuric acid in the filtrate, after acidifying with hydrochloric acid.

According to v. Reis, the method originally devised by Eschka for the determination of sulphur in coke, is also suitable. Mix about 5 grams of iron with about an equal amount of a mixture of 2 parts magnesia and 1 part sodium carbonate ; transfer to a platinum crucible and ignite for 10 minutes in a muffle. Cool the contents of the dish and crush the mass with an agate pestle, re-ignite for 20 minutes, while stirring with a platinum spatula. Cool the mass and boil for about 15 minutes with 100 cc. of water, filter out the insoluble matter and wash it. Oxidize the filtrate with about 5 cc. of hydrogen peroxide, heat, acidify with hydrochloric acid and precipitate with barium chloride.

The colorimetric method of Wiborgh is sometimes used. The principle of the method consists in passing the gases evolved during solution, through a cotton cloth saturated with cadmium acetate, and then comparing the color with that of a similar piece of cloth whose color corresponds to a known content of sulphur.

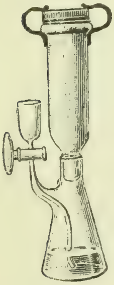

Fig. 45.

Fill the flask, Fig. 45, 1/3 full with water. Boil, to expel the air and then add the sample of iron. Place on the flask the cylinder-formed apparatus having a disk of cotton cloth clamped on the top, and boil to expel the air from the apparatus. Now gradually add dilute sulphuric or hydrochloric acid through the funnel-tube, while the contents are boiling. When the evolution of hydrogen has ceased, boil a few minutes to drive all the hydrogen sulphide through the cloth. Remove the cloth and compare the color with that of similar discs that have been prepared in the same manner with irons of known content of sulphur.

Determination of Phosphorus :—Dissolve from 1–5 grams of iron, according to the amount of phosphorus, in nitric acid, Sp. Gr. 1.20, in a porcelain dish, and evaporate to dryness on the water-bath. Heat the dry salts on the sand-bath until no more oxides of nitrogen are evolved, and then heat for an hour on the hot-plate to destroy all carbon compounds, which would hinder the precipitation of the phospho-molybdate. After cooling, add concentrated hydrochloric acid, digest until all the iron salts are in solution and evaporate again to dryness. Dissolve in dilute hydrochloric acid, filter out the silica and remove the greater part of the hydrochloric acid by evaporation. Dilute the filtrate with water, neutralize with ammonium hydroxide, dissolve the precipitate in nitric acid, warm, and precipitate with ammonium molybdate. See page 41.

The objectionable heating of the residue on the sand-bath to destroy the carbonaceous matter may be avoided by oxidizing the nitric acid solution with chromic acid or potassium permanganate. In the former case, add an equal amount of dilute sulphuric acid to the solution, then add chromic acid and boil for about 10 minutes. If potassium permanganate is used, add the salt gradually to the warm solution and then dissolve the resulting manganese dioxide with the least amount of hydrochloric acid necessary. If chromic acid was used, the precipitate of ammonium-magnesium phosphate may contain chromic oxide. To avoid this, add a few cc. of hydrogen peroxide to the ammoniacal solution, before precipitating with magnesia mixture.

V. Reis found that in the determination of phosphorus in pig-iron, the magnesium pyrophosphate always contained iron. To avoid this, after washing the ammonium phospho-molybdate with dilute nitric acid, drop on the filter from a pipette, 15 cc. of a solution consisting of 10 grams of citric acid dissolved in 100 cc. of ammonium hydroxide, and then wash the precipitate with 2 1/2 per cent. ammonium hydroxide. Dissolve the precipitate in ammonium hydroxide and precipitate with magnesia mixture, as usual.

In phosphorus determinations, many of the operations may be shortened and simplified, according to the degree of accuracy desired. Thus, instead of filtering out the silica, the solution may be diluted to 110 cc., 100 cc. then filtered through a dry filter, and the final result multiplied by 1.1.

The phospho-molybdate precipitate may also be filtered on a dried and weighed filter, washed with 1 per cent. nitric acid, dried for an hour in the air-bath at 120°– to 130° C., and the phosphorus calculated, on the assumption that the precipitate contains 1.64 per cent. of phosphorus.*

In the case of irons low in silicon, the separation of the silica may be omitted ; as the precipitate contains but a relatively small amount of phosphorus, a small amount of contamination causes no serious error. This is especially the case if the iron is high in phosphorus.

[Rapid Volumetric Method for Phosphorus. Titration of the phospho-molybdate precipitate (J. O. Handy) : —Ammonium phospho-molybdate reacts withalkali, according to the following equation :

$$2[(NH_4)_3,12MoO_3,PO_4] + 46NaOH + H_20 = 2[(NH_4)_2HPO_4] + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23H_2O.$$

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* [In the United States, the factor 1.63 is generally used.]

1 cc. of normal alkali=.001348 gram of phosphorus. Make acid and alkali solutions .1484 normal. Then, 1 cc.=.01 per cent. P., when 2 grams are used for analysis. Pemberton, Thilo, Hundeshagen, Manby and Handy worked successfully on the principles upon which the following process is based :

THE METHOD.

The ammonium phospho-molybdate obtained by any standard method, is washed, first with 1 1/2 per cent. nitric acid and then with very dilute potassium nitrate solution until free from adherent acid. Filter and precipitate are then put in a clean vessel and standard sodium hydroxide is then added, until, on stirring, the yellow precipitate is dissolved. Add 1 cc. of phenolphthalein solution, and about 50 cc. of distilled water free from carbon dioxide. Titrate with standard nitric acid to the disappearance of the pink color. The dilution should be roughly proportioned to the amount of phosphorus apparently present ; otherwise, with high phosphorus, the end reaction will not be sharp enough.

SOLUTIONS.

Standard Sodium Hydroxide. Make a saturated solution of sodium hydroxide by agitating a weighed amount with less than an equal weight of water. Allow to cool and clarify in a covered vessel. The clear liquid is free from carbonate (Garrigues' Method). Dilute 25 cc. of this solution to 1 liter with distilled water free from carbon dioxide. Titrate against standard sulphuric acid. Dilute to .1484 N. strength.

Standard Nitric Acid. Dilute 15 cc. of 1.42 nitric acid to 1 liter. Titrate, and dilute as is necessary to make equal to the standard sodium hydroxide.

Phenolphthalein Solution. 1 Gram in 1 liter of neutral 95 per cent. alcohol.

Nitric Acid Wash. Dilute 40 cc. of 1.42 nitric acid with distilled water, to 4 liters.

Potassium Nitrate Wash. Dissolve 4 grams of potassium nitrate in 4 liters of water.

Molybdate Solution. To 1200 cc. of water add 700 cc. of ammonium hydroxide (Sp. Gr. 0.88) and 1 lb. of molybdic acid ; when the molybdic acid is dissolved, add 300 cc. of nitric acid (Sp. Gr. 1.42), and cool. Pour this solution into a mixture of 4800 cc. of water and 2000 cc. of conc. nitric acid. Filter for use after standing 24 hours.

Permanganate solution. 10 grams of $KMnO_4$ in 2 liters of water.

This method is extensively used, and is both rapid and accurate.]

Determination of Carbon.

Total Carbon and Graphitic Carbon are the forms most commonly determined. The carbon contained in iron, other than that in the graphitic form, was formerly called Combined Carbon, and in most cases was estimated by difference, the total carbon and graphitic carbon being determined directly, and the graphitic carbon being left insoluble when the iron was treated with hot acid.

If, however, the iron is treated with cold, very dilute acid, a portion of the chemically combined carbon remains insoluble with the graphitic carbon. This is the carbon which is combined with the iron in the form of carbide. This portion of the carbon, called Carbide Carbon, on treating the iron with hot, strong acid, is partly evolved as hydrocarbons, and partly dissolved, coloring the solution. The carbide carbon may therefore be determined by difference, from the carbon obtained by solution in cold, very dilute acid, and that obtained when the iron is dissolved in hot, strong acid.

If the sum of the graphitic carbon and carbide carbon is subtracted from the total carbon, the difference represents the so-called Temper Carbon, which corresponds to the portion that is evolved as hydrocarbons, when the iron is dissolved in cold acid.

A. Determination of Total Carbon.*

1. Direct Combustion of the Iron in Oxygen :—If the iron is finely pulverized, the carbon can be oxidized to carbon dioxide by direct combustion in a current of oxygen. Mix 4–5 grams, or more, of iron with coarsely granular copper oxide in a large porcelain or platinum boat and place in a porcelain combustion tube. The tube should be sufficiently long to prevent scorching the stoppers. Heat the tube in a combustion furnace such as is used in organic analysis. To decompose the small amount of sulphur dioxide formed from the sulphur of the iron during the combustion, pass the gases through a small U-tube containing a saturated solution of chromic acid, and then through an apparatus to dry and absorb the carbon dioxide. Use a U-tube filled with calcium chloride† and two U-tubes,

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* It should not be forgotten that the filings or turning may have oil adhering to them. The greater part of the oil may be removed by digestion with ether or benzine, and then washing with alcohol. Filings or turning thus purified must be heated for some time at 110°–120° C. Iron perfectly free from oil or other adhering substances containing carbon, can be obtained only by ignition in a current of pure nitrogen.

† The calcium chloride must be tested. See page 57.

filled five-sixths with soda lime and one-sixth with calcium chloride, to absorb the carbon dioxide.*

When the individual parts of the apparatus are connected, gently heat the porcelain tube while passing a slow current of oxygen. When the tube is once warmed, the temperature can be rapidly increased to a red heat. As soon as the iron is at a red heat, the most of the oxygen is consumed in oxidizing the iron; during this time, scarcely any bubbles of gas pass through the chromic acid U-tube. When this oxidation is complete, the carbon begins to oxidize to carbon dioxide, and a regular current of gas passes through the chromic acid U-tube. The combustion should be maintained for 30–45 minutes.

The gain in weight of the soda-lime tube gives the weight of the carbon dioxide, from which the carbon may easily be calculated.

As mentioned above, if this method is used, the iron must be finely pulverized. Some varieties of iron are difficult to pulverize; in such cases, use one of the following methods.

2. Direct Oxidation of the Iron with Chromic Acid:—The apparatus used in this determination, consists of a decomposing flask b, Fig. 46, in which the iron is dissolved in a mixture of sulphuric and chromic acids, and the carbon is oxidized to carbon dioxide. The combustion tube c. of difficultly fusible glass, is filled with copper oxide, and is used to oxidize the hydrocarbons to carbon dioxide and water.†

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* When carbon dioxide which is largely diluted with air or oxygen, is to be absorbed, soda-lime is much preferable to potassium hydroxide, as the latter may fail to absorb all the carbon dioxide, if a large excess of oxygen is present.

† Instead of using a glass tube filled with copper oxide, a looped platinum capillary tube may be used. On passing the gas mixed with air through the heated loop, the hydrocarbons are oxidized to carbon dioxide.

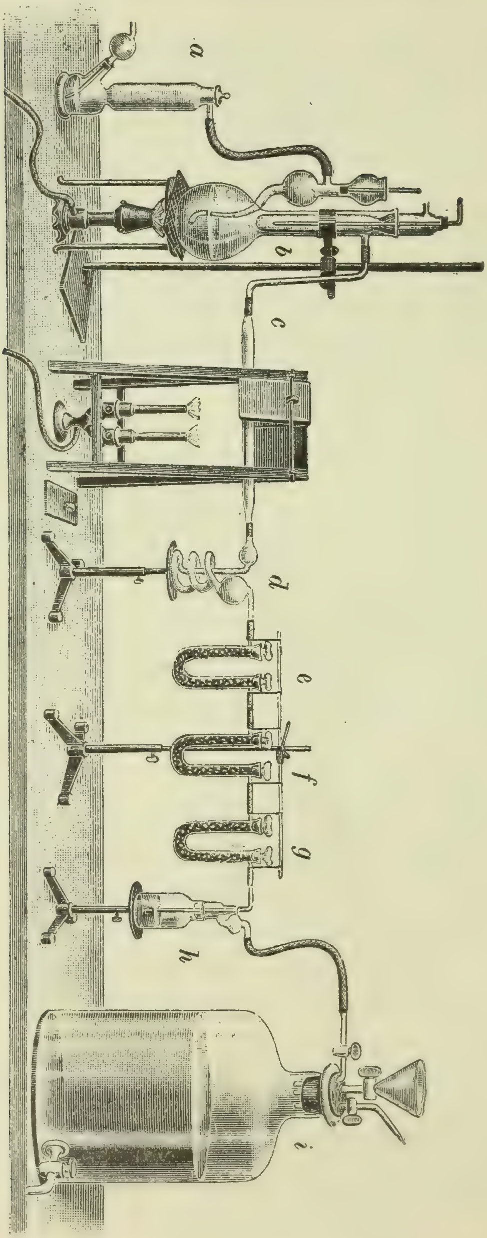

Fig. 46.

The drying apparatus d and e, are filled with concentrated sulphuric acid and phosphorus pentoxide, respectively. The U-tubes, f and g, used to absorb the carbon dioxide, are filled with soda-lime.

The wash-bottle h, filled with concentrated sulphuric acid, is interposed between the aspirator i and the train, to prevent water vapor diffusing backward into the weighed U-tubes f and g. The air is freed from carbon dioxide before entering the train by being passed through the drying-tower a, containing potassium hydroxide and soda-lime.

Disconnect the decomposing flask from the combustion tube, add about 25 cc. of chromic acid solution (180 grams of chromic acid in 100 cc. of water), 150 cc. of copper sulphate solution (200 grams to a liter), and 200 cc. of pure, concentrated sulphuric acid.

The copper sulphate is for the purpose of preventing, as much as possible, the evolution of hydrocarbons and hydrogen.

In rapid determinations in works, igniting the gases may be omitted, and the results obtained, increased 2 per cent. in the case of malleable iron, and 3 1/3 per cent. in the case of pig-iron, as it has been found by experiment that these amounts represent quite accurately the amount of carbon in organic combination.

Heat the above mixture to boiling, and boil for about 10 minutes to destroy organic matter, placing the condenser in the neck of the flask to prevent evaporation. Remove the burner, again connect the flask with the combustion tube, disconnect the weighed U-tubes from the train, and then aspirate air freed from carbon dioxide through the train, at the same time heating the copper oxide. After the aspirator has been removed, connect the soda-lime.

tubes and add the weighed sample of iron (1 gram of pig-iron, 3 grams of malleable iron) in a small glass vessel by means of a platinum wire. Aspirate a moderately rapid current of air through the apparatus, and gradually heat the contents of the flask to boiling. Boil for 2 hours, at the same time passing cold water through the condenser. Extinguish the burners of the combustion furnace, aspirate air through the apparatus for about 2 hours, and reweigh the 2 soda-lime U-tubes. The gain in weight is carbon dioxide.

3. Oxidation of the Carbon previously separated by Copper Chloride:—If coarsely pulverized iron is digested at the ordinary temperature with a solution of perfectly neutral ammonium-copper chloride, all the iron will be dissolved as ferrous chloride, and the carbon will remain insoluble:

$$CuCl_2+Fe=Cu+FeCl_2.$$

50 cc., of a solution of 300 grams of ammonium-copper chloride* in 1 liter of water will be sufficient. To dissolve the precipitated copper, add 15–30 cc. of ferric chloride solution (800 grams Fe_2Cl_6 in a liter of water) :

$$2Cu+Fe_2Cl_6=2FeCl_2+Cu_2Cl_2.$$

Acidify with hydrochloric acid, to dissolve the cuprous chloride formed. Complete solution of the iron may, in some cases, require several hours. Mechanical stirrers greatly hasten the solution. Filter the separated carbon on asbestos or glass wool in a Gooch crucible or carbon tube. The carbon may be oxidized either by heating in a porcelain or platinum boat in a current of oxygen, or by chromic acid as given on page 303. In the latter case, however, a simple apparatus, Fig. 47, devised by the author for the determination of carbon dioxide, may be used. Fill the drying tube between the flask and the absorption tubes, preferably with phosphorus pentoxide, as sulphuric acid always absorbs a small quantity of the carbon dioxide. Place the carbon, together with the as-

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* [Potassium-copper chloride is preferable, as experiments by American members of the International Steel Standards Committee have shown that ammonium-copper chloride is nearly always impure from the presence of hydrocarbons in the ammonium chloride, derived probably from the gas liquor from which ammonium salts are obtained.]

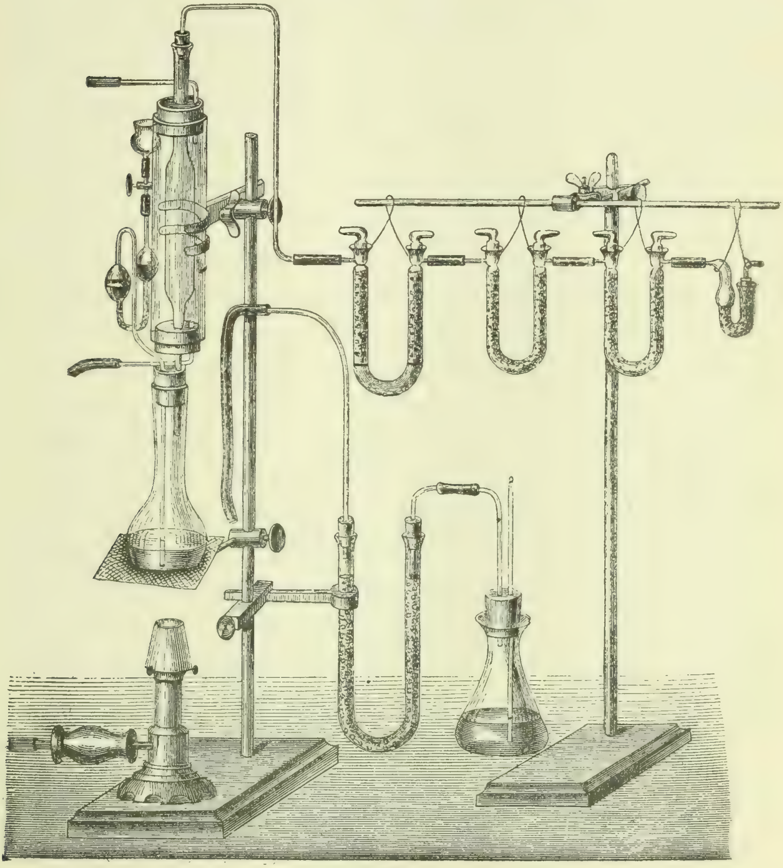

Fig. 47.

bestos on which it was filtered, in the flask, add crystallized chromic acid, (3 grams for each gram of iron) and then add sulphuric acid (2 vols. concentrated acid : 1 vol. water). Connect the flask at once with the rest of the train, and then gently warm the acid.

At the beginning of the experiment, a slow, regular current of air must be aspirated through the apparatus. Gradually increase the temperature of the flask until the contents boil. Continue the boiling for about 15 minutes to expel the carbon dioxide absorbed in the liquid. When the soda-lime tubes are completely cold, determine their weight. The increase in weight is due to carbon dioxide, from which the carbon may be calculated.

4. Oxidation of the Carbon previously separated by Chlorine :—The chromic acid method is, of course, applicable only to those kinds of iron which are decomposable by the acid mixture ; among these are all kinds of malleable iron, ordinary gray and white pig-iron and ferro-manganese. Ferro-silicon, which is rich in silicon, and ferro-chrome, however, are not decomposable by this method. These irons may be decomposed by heating in a current of dry chlorine, by which the chlorides of iron, silicon, phosphorus, sulphur, etc., are volatilized, while carbon, which does not combine with chlorine directly, remains behind.

Place the sample in a porcelain boat, shove the boat into a tube of difficultly-fusible glass, and heat in a combustion furnace. The exit end of the tube should be drawn out smaller and be bent down at a right angle ; immerse the tip in concentrated sulphuric acid to prevent the entrance of air. A sample may be divided between several boats, or several samples may be worked parallel. The air in the apparatus must be replaced by chlorine before heating the tube. First light the burner nearest the exit of the tube, and gradually light the burners one by one, and increase the temperature up to incipient redness,

After all the volatile matter has been expelled, allow the apparatus to cool while passing a current of chlorine. Wash the residual carbon with cold water to remove chlorine and chlorides.

Irons containing chromium, leave a residue of insoluble chromic chloride. This must be reduced to soluble chromous chloride by reduction in a current of hydrogen; a partial reduction suffices, however, since chromic chloride is soluble in chromous chloride.

Filter, and oxidize the carbon as given under 3.

5. [Solution of the Drillings in Potassium-Copper Chloride, and Combustion of the Residue:—Take 3 grams of pig-iron or cast-iron, or 5 grams of wrought-iron or steel, and dissolve in a saturated solution of potassium-copper chloride, and hydrochloric acid, allowing 100 cc. of the solution and 7.5 cc. of acid for each gram of sample. Stir until all the iron is in solution. Cover the beaker and allow to stand for 2–3 hours at a temperature of 60–70° C. Filter on asbestos in a platinum boat, using suction, first moistening the asbestos with hydrochloric acid. The filtrate will be nearly black.

Test the filtrate for carbon by catching a little in a small beaker and adding water; any carbon will appear black; the solution should be pure green on the addition of water.

Wash the carbon 4–5 times with 5 per cent. hydrochloric acid, then with warm water until all the chlorides are removed. If pure water is used at first, cuprous chloride will be precipitated. Dry the boat and carbon at

110° C. and cool in a dissicator. Arrange a combustion train as follows, beginning at the exit end of the combustion tube :

U-tube No. 1 contains 5 grams of silver sulphate dissolved in 10 cc of sulphuric acid. U-tube No. 2 contains granulated copper in the first half, and pumice-stone saturated with anhydrous copper sulphate, in the second half. Prepare the pumice-stone as given on page 56. U-tube No. 3 contains granular calcium chloride in the first half, and glass-wool sprinkled with phosphorus pentoxide, in the second half. The absorption apparatus, containing 1 :1 potassium hydroxide, is next attached. If the potassium hydroxide is too dilute, the solution gives off an appreciable amount of water vapor, owing to its high tension. Attached to the potassium hydroxide bulb is a small U-tube filled with glass-wool sprinkled with phosphorus pentoxide. The last two are the absorption apparatus proper, to be weighed before and after the experiment. The potash bulbs should be refilled after making 3 absorptions. The phosphorus pentoxide should be replaced as soon as it begins to deliquesce. Beyond the absorption apparatus, there should be a guard tube filled with soda-lime, to prevent water vapor diffusing backward from the pump.

To make a combustion, connect the train with a porcelain combustion tube and run a blank for about 3 hours. The absorption bulb will generally show a gain of about 1 milligram per hour, in spite of all precautions. Now place the boat containing the carbon in the combustion tube, attach the weighed absorption bulbs,and gradually heat to a full red heat while aspirating purified air through the train at the rate of about a bubble per second. Maintain the temperature for about an hour, detach the bulbs, cool in the balance case for 20 minutes and weigh. Allow the tube to cool slowly while shutting off the burners one at a time. The increase in weight of the bulbs is CO_2. Wt. $CO_2 \times .2727 =$ Wt.C.]

6. Colorimetric Determination of Carbon (Eggertz): —This method depends upon the fact that the solution of a steel in hot nitric acid is colored darker the more combined (carbide) carbon is present. For the comparison, prepare a solution of steel containing a known amount of combined carbon and dissolve an equal amount of the sample being analyzed. Transfer the solutions to calibrated tubes and dilute the darker solution with water until the 2 tints are alike. The content of carbon in the specimens is then directly proportional to the volumes of the solutions.

Dissolve 1 gram of the steel of known carbon content, which should be approximately near to that of the unknown sample,* and one gram of the latter, in about 2.5 cc. of nitric acid, Sp. Gr. 1.20. The nitric acid should contain no chlorine. Moderate the first action of the acid by dipping the tubes in cold water; finally warm to 80° C., if necessary, to effect solution. The amount of nitric acid should be varied according to the quantity of carbon present. For less than 0.3 per cent., the above amount is sufficient; for 0.3 per cent, use 3 cc. of acid; for 0.5 per cent. carbon use 3.5 cc. acid, and for 0.8 per cent., use 4 cc. acid; for samples higher in carbon, use 5 cc. of acid. If the approximate amount of carbon is unknown, use 2.5 cc. at first, and then add more, if the dark color of the solution or the particles in suspension seem to show that insufficient acid has been used.

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* [The two should have approximately the same physical properties; i. e. should have undergone the same mechanical treatment.]

After solution and cooling, rinse the solutions into calibrated tubes for comparison. The tubes should be provided with glass stoppers to allow thorough mixing.

The colorimetric method is especially suitable as a rapid method in works, and is applicable to all kinds of iron and steel that have not been suddenly cooled or annealed. On the other hand it is not suitable for pig-iron containing graphite.

B. Determination of Graphitic Carbon.

Dissolve 1–3 grams according to the content in graphite[†] in nitric acid, Sp. Gr. 1.18, and heat for about 2 hours on the water-bath. Filter out the graphite, silica, etc., on an asbestos filter, wash with hot water and then with dilute potassium hydroxide, alcohol and ether in succession. Oxidize the graphite in a current of oxygen or with chromic acid, as given above.

C. Determination of Carbide Carbon.

From what has been said on page 301, concerning this form of carbon, it is obtained with the graphite, when the iron is dissolved in cold, dilute acid. Digest 1–3 grams of the sample for 2–3 days at the ordinary temperature, with 10 times the quantity of dilute sulphuric acid (1 :10), while passing a slow current of illuminating gas through the flask to displace the air. Filter, wash, and oxidize as given under **B.**

The difference between the quantity found, and the quantity of graphite, is the carbide carbon.

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[*] Dark-gray pig-iron contains more graphite than that of a light gray color.

D. Temper Carbon.

This form of carbon is best calculated by difference between the total carbon and the sum of the graphitic and carbide carbon.

Determination of Nitrogen.

1. Determination of the Nitrogen which is transformed into Ammonia on solution of the sample in Hydrochloric Acid :—Dissolve the sample in hydrochloric acid in a tubulated retort, and pass the evolved gas through a U-tube partly filled with dilute hydrochloric acid. The latter is for the purpose of retaining any ammonia that might be carried over mechanically with the hydrogen and hydrocarbons. After complete solution, pour the contents of the U-tube back into the retort, add an excess of sodium or calcium hydroxide, and distil as given on page 109.

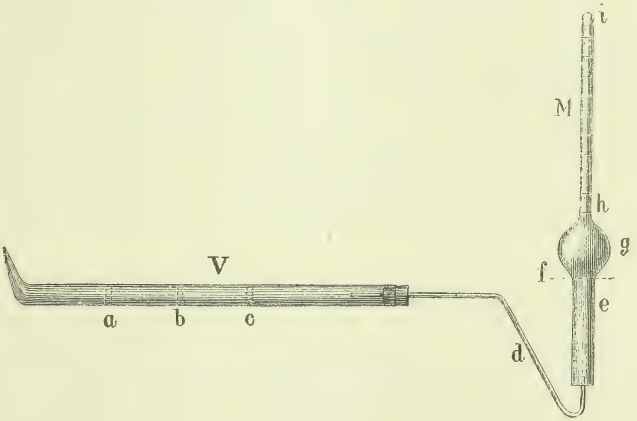

Fig. 48.

Alternative Method (Ullgren) :—Decompose 2 grams of iron with a solution of 10 grams of copper sulphate and

6 grams of sodium chloride; add sodium hydroxide and distil.

2. Determination of the Nitrogen which remains in the insoluble residue after dissolving the Iron (Ullgren):—Fill a combustion tube v, Fig 48, of 30 cm. length, up to a, with about 12 grams of magnesite or sodium bicarbonate, insert a wad of asbestos and then introduce, from a to b, the residue from the iron which is insoluble in hydrochloric acid. The residue should be dried at 130° C. and mixed with about 4 grams of mercuric sulphate. Insert another wad of asbestos at b, and then fill the tube from b to c, with coarse pumice powder which has previously been mixed with mercuric sulphate and water and then dried. Insert an asbestos plug at c and fill the rest of the tube with pieces of pumice stone which have been saturated with a concentrated solution of chromic acid or potassium bichromate, to decompose the evolved sulphur dioxide. By means of the tube d, connect the combustion tube with the measuring tube M, which has an enlargement at g, and is filled with mercury. M has a total volume of about 90 cm. The portion i h, has a capacity of about 40 cc. and the lower portion e, about 30 cc.

Introduce into the tube M with a bent pipette, about 35–40 cc. of potassium hydroxide solution (1:2) and then 15 cc. of concentrated solution of tannic acid, so that the level of the mercury is approximately at f. Now heat the portion of the tube containing the magnesite, to expel the air in the apparatus, allow the gas to pass into M, warm the portion a b, very gently at first, and heat the portion b c to a red heat, now quickly heat the portion a b to a red heat and maintain the temperature until the level of the liquid in M sinks no further.

Finally drive the last traces of the nitrogen over into M by again heating the magnesite. Now remove the tube d, and transfer M by means of small dish filled with mercury to a wide, deep cylinder filled with water. The mercury, potassium hydroxide solution, and tannic acid solution, are displaced by water owing to the differences in specific gravity. Close the tube with the thumb or with a rubber stopper and rinse the potash solution from the tube. Transfer the tube to the jar filled with pure water, and after 15–20 minutes note the height of the barometer and the temperature of the water. Now clamp the tube so that the level within and without the tube is the same, and read the volume of the nitrogen.

Let V represent the volume of the nitrogen found, V′ the volume of the same quantity of nitrogen at 0° C and 760 mm. barometric pressure, B the height of the barometer in millimeters, t the temperature of the water in degrees centigrade and f the tension of water vapor at the observed temperature. Then:

$$V' = \frac{V(B-f)\,273}{760(273+t)}.$$

WELL, SPRING, AND RIVER WATER.*

The constituents determined in an ordinary water analysis, depend upon whether the water is to be used for domestic or manufacturing purposes. In the consideration of a water to be used for drinking purposes, iron, calcium and magnesium oxides, alkalies, sulphuric acid, hydrochloric acid, nitric acid, nitrous acid, carbonic acid, ammonia, organic matter and total solids, are generally determined ;* while for manufacturing purposes, the only constituents of interest are the alkaline earths, total and permanent hardness, ferrous iron, sulphuric acid, hydrochloric acid and total solids.†

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* [On the Bacteriological examination of water, see: Micro-Organisms in water, Percy and G. E. Frankland. Manual of Bacteriology, Dr. G F Sternberg. Microscopy of Drinking Water, G. E. Whipple, N. Y., 1899.]

Determination of Total Solids, Ferrous Iron, Calcium, Magnesium, and Alkalies :—Evaporate 500–1000 cc. of the water to dryness on a water-bath in a weighed platinum dish, and heat the residue in an air-bath or oil-bath at a temperature of 120–125° C., to constant weight. Dissolve the residue in dilute hydrochloric acid, covering the dish to avoid loss by effervescence. Heat the solution as long as carbon dioxide is evolved, rinse off the cover and evaporate again to dryness. Dissolve the soluble salts in dilute hydrochloric acid, filter out the sillca, if any is present, and wash it with hot, dilute hydrochloric acid.

Precipitate the iron in the filtrate by adding ammonium hydroxide to alkaline reaction ; filter out the ferric hydroxide, dissolve in hot, dilute hydrochloric acid and repeat the precipitation. This double precipitation is always necessary, especially if the water contains much calcium salts, as calcium carbonate is always precipitated with the ferric hydroxide.

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* A good drinking water should contain in 100,000 parts:
a. Not more than 50 parts solid residue.
b. " " " 18–20 parts $CaO + MgO$.
c. " " " 8–10 parts SO_3.
d. " " " 3–5 parts $NaCl$ or 2–3 parts Cl.
e. " " " 0.5–1.5 parts N_2O_5.

The amount of organic matter should correspond to not more than 1 part $KMnO_4$. See below. Ammonia and nitrous acid should not be present in more than mere traces.

† For the determination of all the constituents present, see analysis of Mineral Water.

The precipitated ferric hydroxide contains a small amount of silica, and all the alumina and phosphoric acid. The quantitative determination of the latter is not necessary in the present case; however, the determination of the iron may be of importance, especially if the water is to used for manufacturing purposes. Dissolve the precipitate in dilute hydrochloric or sulphuric acid, reduce the iron to the ferrous condition and titrate with permanganate.

In determining very small amounts of iron, it is necessary to use a very dilute solution of permanganate; e. g., a solution corresponding to 0.001 gram of iron per cubic centimeter.

In the case of well water containing considerable iron, a fresh sample may be drawn from the well, acidified with sulphuric acid, and titrated directly with permanganate, as a check on the determination of iron in the regular course of analysis. In this case, the amount of permanganate necessary to permanently redden an equal volume of distilled water must be determined, and subtracted from the amount required in the above direct titration.

Add ammonium oxalate in excess to the filtrate from the ferric hydroxide, filter out the calcium oxalate and determine it as given on page 21.

To separate magnesia from the alkalies, proceed as given on page 105.

Determination of Alkalies:—Add dilute sulphuric acid to the filtrate from the magnesia and evaporate to dryness on the water-bath. Gently ignite the residue to volatilize the sulphuric acid and the ammonium salts, and then add solid ammonium carbonate and re-ignite to form normal sulphates. See page 106. Cool in the dessicator and weigh. If it is desired to separate potassium from sodium, proceed as given on page 106.

In the examination of a water that is to be used for manufacturing purposes, the determination of calcium and magnesium is frequently omitted, and the amount of standard soap solution required to produce a permanent lather in a definite volume is determined. This determination is empirical, and gives what is called the 'hardness' of the water.

When a soap solution is added to water containing calcium and magnesium salts in solution, the calcium and magnesium are precipitated as the insoluble salts of the fatty acids contained in the soap.

As soon as the decomposition is complete, a slight excess of the soap solution produces a permanent lather, if the flask is agitated. This formation of a lather is the end reaction.

The number of parts of calcium oxide contained in 100,000 parts of a water, is called its 'hardness.'* A water which shows a degree of hardness of 15, therefore contains 15 parts of calcium oxide in the form of sulphate, carbonate, nitrate, etc., in 100,000 parts of the water.†

As is well known, the greater part of the earth carbonates is precipitated on boiling the water, owing to the decomposition of the bicarbonates, while the sulphates and chlorides remain in solution. It is customary, therefore, to speak of 'total hardness,' by which is meant the entire amount of alkaline earths present, and 'permanent hardness,' which gives the amount of the alkaline earths remaining in solution after boiling the water. The difference between the two is called the 'temporary hardness'; the latter corresponds approximately to the amount of bicarbonate in solution.

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* [This is the German standard. The French standard is stated in terms of milligrams of calcium carbonate in one hundred grams of water, or part calcium carbonate per 100.000 parts of water. The English standard represents grains of calcium carbonate per gallon of 70.000 grains The American standard represents grains of calcium carbonate per gallon of 58,381 grains.]

† Magnesiun oxide corresponds to an equivalent quantity of calcium oxide.

Determination of Total Hardness. Clark's Method :—The standard soap solution is made of such a strength that 45 cc. corresponds to 12 mg. of calcium oxide in 100 cc. of water. The soap is prepared as follows: Rub together 150 parts of lead plaster and 40 parts of potassium carbonate. Extract the mass with alcohol, filter, evaporate the filtrate on the water-bath, and redissolve in alcohol. Dissolve 2 parts of the soap in 100 parts of dilute alcohol, (56° Tr).

Standardize the soap solution against a solution of barium chloride as follows: Dissolve 0.523 gram of dry barium chloride in water and dilute to a liter. Place 100 cc. of this solution in a stoppered vessel of about 200 cc. capacity, and run in the soap solution from a burette until a permanent lather results on shaking the mixture.

Dilute the soap solution with sufficient alcohol to make 45 cc. correspond to 100 cc. of the barium chloride solution; then, 45 cc. of the soap solution correspond to a solution of 12 mg. of calcium oxide in 100 cc. of water.

To determine the total hardness of a water, proceed exactly as in standardizing; add the soap solution drop by drop from a burette to 100 cc. of the water in a flask, until a permanent lather is obtained on shaking the flask. If the water shows a hardness of more than 12, the end reaction is uncertain, and in such a case, it is better to repeat the titration, using a more dilute solution. Take 10 cc. of the water, dilute to 100 cc. with distilled water and proceed as given above.

Determination of Permanent Hardness:—Boil 400–500 cc. of the water for at least 30 minutes, replacing the evaporated water with distilled water. After cooling, filter out the precipitated carbonates, and dilute the filtrate to exactly the same volume as was taken for analysis. Take an aliquot part, e. g., 100 cc. and determine the hardness as given above.

The table of Faisst and Knauss given in the back of the book, gives a direct reading of the degree of hardness from the number of cubic centimeters of soap solution used, provided 100 cc. of water was taken for analysis.

If the number obtained by titration is not contained in the table, note the number in the table that comes nearest to the number found and multiply the difference between the two numbers by the fraction of a degree of hardness corresponding to 1 cc. of the soap solution. The product thus obtained is subtracted from, or added to, the degree of hardness corresponding to the number in the table, according to whether the number of cubic centimeters of soap solution found by titration is subtracted from the number in the table, or the latter from the number of cc. found by experiment.

If, for example, 36 cc. of soap solution were used, multiply the difference between 36 and 36.7, 0.7, by 0.294; the product is 0.2. In this case, then, 0.2 is to be subtracted from 9.5, and a hardness of 9.3 is obtained. Again, if 100 cc. of the water required 44 cc. of the soap solution, multiply 44–43.4, 0.6, by 0.31, and add the product to 11.5. The water, then, has a hardness of $11.5 + 0.186 = 11.7$ degrees.

Determination of Hydrochloric Acid:—This determination may be made either gravimetrically, weighing the chlorine as silver chloride, or volumetrically, with standard silver nitrate. The gravimetric method has been given above. See page 26. For the volumetric method, see: Volumetric Analysis. The quantity of water that should be taken for the sample, depends upon the amount of chlorine compounds in the water. If but a trace is present, a large quantity of the water should be concentrated by evaporation, especially if the gravimetric method is used.

Determination of Sulphuric Acid:—Use from 500–1000 cc. of water, acidify the water with hydrochloric acid and precipitate with barium chloride. If the qualitative test has shown but a small amount of sulphuric acid in the water, a large sample should be concentrated, after acidifying with hydrochloric acid.

When comparing several well waters, and extreme accuracy is not required, the sulphuric acid may be more quickly determined volumetrically. Use a standard solution of barium chloride containing 12.2 grams of dry barium chloride per liter. Make up a solution of potassium chromate of equivalent strength, by dissolving 7.365 grams of dry potassium bichromate in 100 cc. of water.

Add to this solution, sufficient ammonium hydroxide to change the color from red to yellow, forming ammonium-potassium chromate. Dilute to 1 liter. 1 cc. of the barium chloride solution corresponds to 1 cc. of the ammonium-potassium chromate solution.

Boil the water for a long time, to decompose the bicarbonates of the earths and precipitate the normal carbonates; replace the evaporated water with distilled water. Filter, boil the filtrate and precipitate with an excess of the standard barium chloride solution, of which 10 cc. generally suffices. The excess of barium may now be titrated back with ammonium-potassium chromate; add the latter from a burette until the supernatant liquid appears of a pale yellow color. Tiemann* recommends a colorimetric method for estimating this slight, necessary excess of chromate. Dilute the liquid to a definite volume, e. g. 150 cc. (Tiemann makes the precipitation in a graduated flask), filter off 100 cc. through a dry filter† into a cylinder of colorless glass. Place 100 cc. of distilled water in a similar cylinder, and add standard chromate solution drop by drop from a burette until the tint is the same in the two cylinders. The quantity of stand-

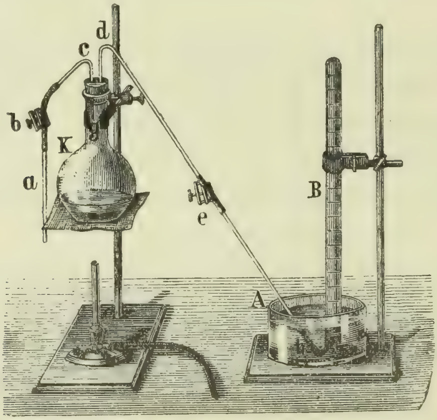

Fig. 49.

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* Ber. deutsch, chem. Gesell, Vol. 6, p. 920.

† [The first few drops must be rejected, owing to adsorption of the salts by the paper.]

ard chromate shown by the comparison, is to be subtracted from the amount used in the precipitation.

Determination of Nitric Acid. Schulze's Method, modified by Tiemann :*—The method depends upon the decomposition of nitrates by hydrochloric acid and ferrous chloride, and measurement of the nitric oxide formed :

$$6FeCl_2+6HCl+2HNO_3=3Fe_2Cl_6+4H_2O+2NO.$$

Use the apparatus shown in Fig. 49. K is a flask of about 150 cc. capacity which is closed with a 2-hole rubber stopper ; through one hole, the tube c. g. passes, and through the other hole, the tube d. Both tubes are provided with screw pinch-cocks at b and e, respectively.

The bent end of the tube e h, should be covered with a piece of rubber to guard against breakage. The tube c g is drawn out to a fine opening, about 2 cm. below the cork, and the other tube bare projects below the cork. A is a glass dish containing 10 per cent. sodium hydroxide, B a measuring tube divided into tenths of cubic centimeters and filled with boiled sodium hydroxide.

Concentrate 100–300 cc. of the water to about 50 cc. in a porcelain dish, rinse the water and precipitated earth carbonates into the flask K, and continue the concentration ; toward the end of the operation, immerse the tube e h in the sodium hydroxide. When the air is completely expelled from the apparatus, the sodium hydroxide will quickly suck back through the tube e h. The rubber tubing at e should be held between the fingers during the expulsion of the last traces of air, to allow closing the tube at the proper moment.

Close the screw pinch-cock e, and continue the boiling (allowing the water vapor to escape through the tube g a) until the volume is reduced to about 10 cc., then remove the flame, close the pinch-cock b, and fill the arm a b with water, Care must be taken that no bubbles of air enter b. Now place the graduated tube B over the end of the tube e h so that the latters enters B about 2–3 cm. When a vacuum is produced in K by the condensation of the water vapor, (shown by the collapsing of the tubes at e and b), pour about 20 cc. of a nearly saturated solution of ferrous chloride into a small beaker, immerse the tube a b, open the pinch-cock b and allow the liquid to flow into the flask. Through the same arm, add two small portions of concentrated hydrochloric acid and then close the pinch-cock. Gently warm the flask until the pressure inside and outside is the same, (shown by the collapsed tubes) open the pinch-cock e, and pinch together the rubber tubing with two fingers until there is sufficient pressure to force the nitric oxide over into B. When the evolution of gas becomes weak, heat the solution, gently at first, and then more strongly, until the level in B does not change. Finally, nothing but hydrochloric acid gas passes over, and produces a slight noise by its absorption in the sodium hydroxide. Remove the tube e h, transfer the tube B to a cylinder of water, and proceed as given on page 315.

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* Ber. deutsch. chem. Gesell. Vol. 6, p. 1041.

Multiply the number of cubic centimeters of nitric oxide found by the formula on page 315, by 2.413, which gives the equivalent amount of N_2O_5.

This method is applicable even if the water contains large amounts of dissolved matter. Care must only be taken that the quantity of water used for analysis contains at least 3 mg. of N_2O_5, otherwise a larger amount of water must be concentrated by evaporation.

Determination of Nitrous Acid. Trommsdorff's Method :—If potassium iodide, starch solution, and dilute sulphuric acid are added to the solution of a nitrate, the blue color of iodide of starch is produced* which is more or less intense according to the amount of nitrous acid present. The amount of nitrous acid present, may be determined colorimetrically by treating a similar quantity of distilled water, under the same conditions, with a measured amount of a solution of potassium nitrite.

As the potassium iodide-starch solution soon becomes unfit for use, a zinc iodide-starch solution is used instead. The latter should be placed in tightly stoppered bottles, and if kept in the dark may be used for a long time.

Besides the zinc iodide-starch solution, a solution of potassium nitrite of known strength is required.

Preparation of the Starch Solution : Disintegrate 5 grams of starch in a little water, add to a boiling solution of 20 grams of zinc chloride in 100 cc. of water, cover the dish and boil until the starch is completely dissolved ; add 2 grams of dry zinc iodide, dilute to a liter and filter. Before using the solution, it must be tested by diluting with water and adding dilute sulphuric acid, to see if it is colored blue.

Preparation of the Potassium Nitrite Solution :—Precipitate a concentrated solution of potassium nitrite with silver nitrate ; filter off the silver nitrite, wash with cold water, dissolve in the least amount of boiling water necessary and purify by crystallization. Dry the crystals between filter paper, weigh out 0.406 gram, dissolve in hot water, add potassium or sodium chloride as long as precipitation ensues, and dilute to 1 liter without filtering out the silver chloride. When the precipitate has settled, pipette out 100 cc. of the clear solution and dilute to 1 liter. 1 cc. of this solution contains 0.01 mg. of nitrous acid.

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* $N_2O_3 + 2HI = H_2O + 2NO + I_2$.

To determine the content of nitrous acid in a water, transfer 100 cc. of it to a narrow cylinder of colorless glass, whose dimensions are so chosen that this quantity forms a layer 18–20 cm. in thickness. Add 3 cc. of the zinc iodide-starch solution and 1 cc. of dilute (1 :3) sulphuric acid. If the iodide of starch color shows at once, or after a short time, the experiment must be repeated, using 10–15 cc. of the water, and diluting to 100 cc. with distilled water. The iodide of starch color should not show until after several minutes.

Measure 100 cc. of distilled water in each of 2–4 cylinders of the same dimensions, add 1–4 cc. of potassium nitrite solution, 3 cc. of zinc iodide–starch solution and 1 cc. of dilute sulphuric acid. Now compare the tints of the 4 cylinders with the tint of the unknown water. The comparison can best be made by standing the cylinders on white paper and looking down through the column of liquid. If the tint of the unknown water is not the same as one of the four standards, the latter must be varied by using different amounts of the nitrite solution, until the standard and the unknown agree in tint.

This method gives reliable results only when the amount of nitrous acid in 100 cc. of water is within the limits of 0.01–0.04 mg.

When many colorimetric analyses are required to be made, the Duboscq colorimeter, Fig. 50, facilitates the work. This apparatus is so arranged that the thickness of the layer of the solution may be varied until it shows the same tint as the standard. Place the solution to be tested in the cylindrical vessel g and the standard in g′; in the two vessels are immersed adjustible cylinders, b and b′, the bottoms of which are closed with glass discs; b and b′ are movable by a rack and pinion adjustment which is provided with a vernier, so that the distance between the disc b and the bottom of g can be accurately measured. The light reflected through the colored liquids by the mirror S, is again reflected by P and P′ in such a manner that on looking through the telescope O, one-half of the field is colored by one solution and the

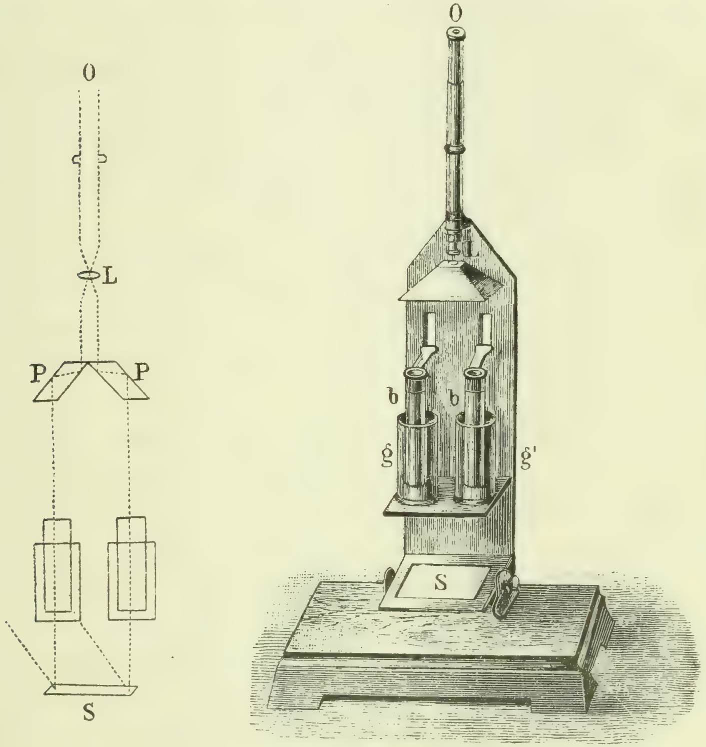

Fig. 50.

other half by the other solution.

By varying the positions of the two cylinders, b and b′, the two halves of the field of view may be made to agree in tint.

The concentrations of the two solutions are then inversely as the thickness of their layers below b and b′.

Method of Feldhauser—Kubel :—This method is based upon the oxidation of nitrous acid to nitric acid by potassium permanganate. An excess of permanganate is added, and the excess titrated back with a standard solution of ammonium-ferrous sulphate.

This method is especially to be recommended if the nitrous acid amounts to more than 1 mg. in 100 cc. of water ; the results are inexact, however, if the water contains less than 0.1–0.2 mg. of nitrous acid in 100 cc. of water. (Tiemann.)

Use a solution of permanganate about N/100 in strength, containing 0.34—0.36 gram of potassium permanganate per liter. The ammonium-ferrous sulphate solution should contain 3.92 grams of the dry salt in 1 liter. Adjust the permanganate solution so that 1 cc. corresponds to 1 cc. of the ammonium-ferrous sulphate solution ; 1 cc. of the permanganate solution then corresponds to 0.19 mg. of nitrous acid.

The method, in general, is similar to the standardization of permanganate. See : Volumetric Analysis ; Potassium Permanganate and Ferrous Salts. Add an excess of the standard permanganate solution to 100 cc. of the water, 5 cc. of dilute (1 :3) sulphuric acid, and titrate back with the ammonium-ferrous sulphate solution.

The temperature of the water during the titration should be between the limits 15–25° C. ; if it is above

25°, organic matter may be oxidized, if below 15°, the nitrous acid may not all be oxidized.

Determination of Ammonia. Method of Frankland and Armstrong: —This method depends upon the behavior of ammonia, or its salts, towards potassium-mercuric iodide.

The ammonia is determined colorimetrically. The method presupposes the absence of those constituents (iron, calcium, magnesium, etc.) that are precipitable by the alkaline potassium-mercuric iodide solution. These constituents may be removed by adding sodium carbonate and sodium hydroxide (1 part NaOH : 2 parts water), and filtering. All chemicals used must be free from ammonia or ammonium salts.

Prepare a standard solution for comparison, by dissolving 3.147 grams of dry ammonium chloride in 1 liter of water; dilute 50 cc. of this solution with water to 1 liter ;1 cc. contains 0.05 gram of ammonia.

Preparation of Potassium-Mercuric Iodide. Nessler's Reagent :—Dissolve 50 grams of potassium iodide in 50 cc. of hot water and add a hot concentrated solution of mercuric chloride (20–25 grams) until a permanent red precipitate of mercuric iodide is formed. Add 300 cc. of potassium hydroxide (1 :2), and dilute to 1 liter.

To determine ammonia, pour 300 cc. of the water to be tested into a glass cylinder, add 2 cc. of sodium carbonate and 1 cc. of sodium hydroxide (1 :2), stopper and shake. When the precipitate has settled, pipette 100 cc. of the clear water into a tall, narrow glass cylinder (see determination of nitrous acid), and add 1 cc. of Nessler's reagent. If a dark reddish-yellow or reddish color is produced, there is too much ammonia present for an accurate determination, and less must be taken (5–50 cc.) and diluted with distilled water to 100 cc. The reagent should produce a bright yellow color. Proceed as given in the determination of nitrous acid. Add 0.2–2 cc. of the standard ammonium chloride solution and 1 cc. of Nessler's reagent, and compare the colors. See page 326.

This method is reliable only within the limits 0.005–0.1 mg. ammonia in 100 cc. of water (Tiemann). If more than this quantity is present, the water must be correspondingly diluted with distilled water.

For another method of determining ammonia, see analysis of Mineral Water.

Determination of Organic Matter.* Kubel's Method :—

This method depends upon the oxidation of the organic matter by potassium permanganate in acid solution. The excess of the permangangate is titrated back with oxalic acid. A solution of permanganate containing 0.32–0.34 gram of the crystallized salt in a liter, is used ; this is standardized against N/100 oxalic acid, prepared by dissolving 0.608 gram of pure crystallized oxalic acid in a liter of water. The same conditions must be observed in standardizing and in the actual titration.

Place 100 cc. of distilled water in a flask of about 300 cc. capacity, add 5 cc. of dilute (1 :3) sulphuric acid and heat to boiling. Add from a burette, 3–4 cc. of the permanganate solution, boil for 5 minutes, remove the burner and reduce the permanganate with 10 cc. of N/100 oxalic acid. Titrate the excess of oxalic acid with permanganate.

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* Another method of determining organic matter, consists in evaporating the water to dryness, heating the residue to 120°—140°C., weighing, and then burning off the organic matter. As the earth carbonates lose carbon dioxide on ignition at a red heat, the ignited residue is moistened with ammonium carbonate and dried to constant weight at 130°—140°C. It is apparent that ignition of the residue not only burns off organic matter, but also volatilizes ammonium compounds, decomposes nitrates, etc.; a portion of the calcium carbonate may also be decomposed by the silica, and magnesium chloride may decompose to form magnesia and hydrochloric acid etc.

In the calculation, it should be remembered that the 10 cc. of oxalic acid added contained 6.28 mg. of crystallized oxalic acid ($H_2C_2O_4+2H_2O$) and that this corresponds to 3.16 mg. of potassium permanganate, or 0.8 mg. of oxygen, (required to oxidize the oxalic acid to carbon dioxide).

To determine the organic matter in a sample of water, proceed as given in the standardization. Use 100 cc. of the water to be tested. Of course, if 3–4 cc. of permanganate solution is not sufficient to oxidize all of the organic matter, more must be added; in all cases, sufficient must be added to leave a permanent red color after boiling.

The excess of permanganate over that required to oxidize the oxalic acid, represents the amount necessary to oxidize the organic matter present in the sample.

If x represents the number of cubic centimeters of permanganate that corresponds to the 10 cc. of oxalic acid used, y the number of cubic centimeters of permanganate reduced by the organic matter, then $\frac{3.16 \cdot y}{x}$ represents the number of parts of permanganate, and $\frac{0.8 \cdot y}{x}$ the number of parts of oxygen, which were necessary to oxidize the organic matter in 100,000 parts of the water.

If, for example, 100 cc. of water required 7.2 cc. of permanganate to give a permanent red color, 10 cc. of oxalic acid were then added and 3.5 cc. of permanganate were required to titrate back, and if 10 cc. of the oxalic acid corresponds to 8.5 cc. of the permanganate solution, then:

$7.2+3.5=10.7$; $10.7-8.5=2.2$ cc. of permanganate.

100,000 parts of the water, therefore, required for oxidation of the contained organic matter:

$\frac{2.2 \,.\, 3.16}{8.5} = 0.8179$ parts of permanganate, corresponding to $\frac{2.2 \,.\, 0.8}{8.5} = 0.2070$ parts of oxygen.*

If the water being examined contains nitrous acid, the latter will also be oxidized. See page 328. For each part of nitrous acid in 100,000 parts of water, 1.66 parts of permanganate must be subtracted. If the water contains ammonia or hydrogen sulphide, evaporate to about 2/3 the original volume, and replace the evaporated water by distilled water before titration.

Schulze's Method:—This method differs from that of Kubel in that the oxidation is effected in alkaline solution. After acidifying with sulphuric acid, the excess of permanganate is reduced with 10 cc. of oxalic acid, and the excess of the latter titrated with permanganate.

Proceed as given above. Add 1/2 cc. of sodium hydroxide† to 100 cc. of the water, and then add 10–15 cc. of permanganate solution, according to the amount of organic matter present.

Boil the water for about 10 minutes, after which the red color must still persist; cool to 50–60° C., add 5 cc. of dilute sulphuric acid (1 :3) and 10 cc. of the oxalic acid. Titrate back with permanganate, and calculate as in the other method.

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* Kubel and Wood assume that 5 parts of organic matter are oxidized by 1 part of permanganate; the excess of permanganate, in milligrams, multiplied by 5, then gives the content of organic matter in 100,000 parts of water. This supposition does not agree with the results of Tiemann's experiments. Tiemann found that the absolute weight of the non-volatile organic matter in different waters had a varying relation to the amount of permanganate necessary to oxidize the organic matter.

† Prepared from sodium. Dissolve 1 part sodium hydroxide in 2 parts of water.

In reporting the results of an analysis, it is always more correct to report the constituents found in the analysis, in the uncombined state, than to report them combined as compounds. Thus, simply the number of parts of chlorine, Cl, sulphuric acid, SO_4, nitric acid, NO_3, nitrous acid, NO_2, silica, SiO_2, calcium, Ca, sodium, Na, etc., in 100,000 parts of the water, should be given. Every method of combining the metals with the acids is more or less arbitrary; suffice it to say that chlorine is generally combined with sodium and any excess combined with potassium. If there is more than sufficient chlorine for both sodium and potassium, the excess is combined with calcium. If, on the other hand, the chlorine does not suffice to neutralize the alkalies, the latter are calculated as sulphates. The remainder, or all of the sulphuric acid, is then combined with calcium, and the excess of calcium and the magnesium calculated as bicarbonates. If the water contains nitric acid, this is generally first united with ammonia and any excess combined with calcium. Nitrous acid is likewise united with ammonia. If the water contains iron in sufficient quantity to be determined, it is likewise calculated as carbonate. The silica is generally reported in the uncombined form.

MINERAL WATER.

1. WORK AT THE SPRING.

First determine the physical relations of the spring, especially as to appearance, odor, and taste of the water.

The rate of efflux, and the temperature of the water, together with the temperature of the air, should be noted. It is also necessary to test the reaction of the water with blue and red litmus paper, and to notice whether any change of color in the paper remains the same on drying the latter. If the spring, or its exit, contains muddy deposits or solid incrustations, samples of them should be collected and placed in stoppered bottles, and preserved for examination.

Determination of Hydrogen Sulphide :—This constituent may easily be detected by its odor, or by its decolorizing effect on weakly blued iodide of starch paper when a quantity of the water is acidulated with sulphuric acid and shaken in a flask.

The amount of hydrogen sulphide is determined with a standard iodine solution ; a solution containing 1 gram of iodine (dissolved in potassium iodide) in a liter, is a convenient strength. Measure a quantity of the water, add acetic acid, and fresh, dilute starch solution, and then add the iodine solution, drop by drop while stirring, until the blue color of iodide of starch shows. If the amount of iodine necessary to oxidize the hydrogen sulphide by the above method has been determined, it is advisable to repeat the experiment, as follows : Place almost the necessary amount of iodine solution in a beaker, add the same quantity of water as before, and mix. Now add a few drops of acetic acid, a little starch solution, and titrate to the end reaction with iodine solution.

The amount of iodine solution required to give the same end reaction with the same amount of distilled water, starch and acetic acid, should now be determined, and subtracted from the amount found in the analysis proper.

In the case of warm springs, the hydrogen sulphide can be determined with iodine solution only after the water has become perfectly cold; the cooling may be hastened by immersing the flask in cold water. The air absorbed while filling the flask, may decompose part of the hydrogen sulphide; it is therefore advisable to previously fill the flask with pure carbon dioxide and to remove the stopper only after immersing the flask.

If it is desired to determine the hydrogen sulphide gravimetrically, add a solution of silver chloride in sodium thiosulphate, to which has been added a little ammonium hydroxide, to a portion of the water, and stopper the flask. This operation should be done at the spring. Filter out the precipitate later at the laboratory, and oxidize the sulphur with hydrogen peroxide, or bromine water, expel the bromine from the filtrate and determine the sulphuric acid as usual.

To accurately determine sulphuric acid in a mineral water containing hydrogen sulphide, it is necessary to either boil a sample of the water with hydrochloric acid at the spring, or to precipitate the sulphur compounds with cadmium chloride in closed flasks. The sulphuric acid may then be determined in the filtrate from the cadmium sulphide.

The precipitate produced by the cadmium chloride may also be used to determine the free and combined hydrogen sulphide. Oxidize the precipitate with hydrogen peroxide or fuming nitric acid, and determine the sulphuric acid as usual. If nitric acid was used for oxidation, the excess should be evaporated.

If the water contains thiosulphuric acid, it may also be determined in the filtrate from the cadmium sulphide.

Precipitate 2 portions of the water with a solution of cadmium chloride, filter, warm the filtrate and add an excess of silver nitrate. Filter out the resulting precipitate of silver sulphide* and silver chloride, dissolve the chloride with ammonium hydroxide, and the sulphide in nitric acid. Expel the excess of nitric acid from the solution of the silver sulphide, and precipitate the silver as chloride. 1 molecule of silver chloride corresponds to 1 molecule of thiosulphuric acid.

Determination of Ferrous Iron:—For this determination, use a solution of potassium permanganate that contains about 0.6 gram of the crystallized salt in a liter. Acidify 500 cc. of the water with dilute sulphuric acid, and titrate with the previously standardized permanganate. Stand the beaker on a piece of white paper and observe the color by looking down through the solution. Determine the number of cubic centimeters of permanganate solution that is necessary to produce the same tint in the same volume of distilled water, and subtract from the amount necessary to oxidize the ferrous iron.

This method is not applicable to waters that contain hydrogen sulphide; in such a case, the iron must be determined gravimetrically, See below.

Determination of Total Carbon Dioxide:†—For this determination there is needed a solution containing 1 part of crystallized calcium chloride in 5 parts of water, to which has been added 10 parts of ammonium hydroxide, Sp. Gr. 0.96. This solution must be prepared several weeks before using, and should be kept in closely stoppered flasks. Fill a measuring flask of 200–1000 cc. capacity with the mineral water, according to the amount of carbon dioxide contained, immerse as far as possible below the surface of the water, and suck the water from the flask by means of a rubber tube, so that the flask may be filled with water from below. Pour the contents of the measuring flask, together with a sufficient amount of the clear, calcium chloride solution, into a second flask suitable for transportation, rinse out the measuring flask several times with boiled distilled water and carefully stopper with a cork. The cork should be moistened with distilled water and have a piece of rubber gauze drawn over it before being inserted. (Bunsen).

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* $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$.

† For the collection and analysis of gases absorbed in water, see Bunsen, Gasometrischen Methoden, and W. Hempel, Gasanalytischen Methoden, or translation of the latter work, by L. M. Dennis.

Determination of Specific Gravity :—If the mineral water contains a large amount of gas, it is advisable to fill the specific gravity bottle at the spring. The flask shown in Fig 51, recommended by Fresenius, is used ; it has a capacity of 200–400 cc. The neck is drawn out to a length of about 50 mm. and a diameter of 5–6 mm., and is provided with a millimeter scale. The mouth of the flask is round and can be tightly closed with a rubber stopper.

To fill the flask, close its mouth with the thumb, immerse as deep as possible in the water and allow to fill until the neck is about half full.

Close the mouth of the flask with the thumb, remove from the water and stopper at once with a rubber stopper. To ensure safety, secure the stopper in place with a string.

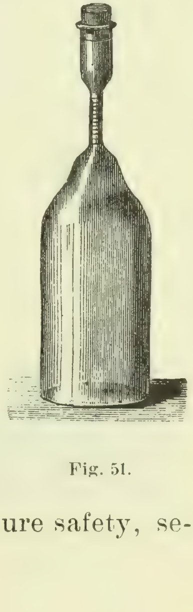

Fig. 51.

Filling the Bottles :—Ordinary wine bottles may be used in which to ship the water to the laboratory. Immerse the bottle as deep as possible into the water, empty and refill. Stopper the bottles with good corks, over which has been drawn sheet rubber ; cut off the projecting end of the cork, and seal when dry.

If a more minute examination is to be made, fill a few carboys with the water.

2. DETAILS OF THE ANALYSIS.

Determination of Specific Gravity :—If the specific gravity flask was filled with water at the spring, fill a similar flask with distilled water, stopper, and allow the two flasks to stand together for at least 12 hours so that they may have the same temperature.

Note the height of the liquid in the graduated neck of the flask containing the mineral water, and weigh. Empty the flask, rinse it out and then fill to the same mark with water from the second flask, and weigh again. Now empty the flask, rinse it out with alcohol and ether, dry, and determine its weight.

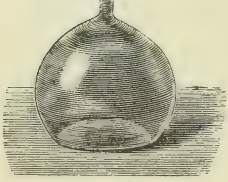

Fig. 52.

The flask should be carefully cleaned and dried on the outside before weighing.

If the flask was not filled at the spring, an ordinary pyknometer, Fig. 52, may be used.

Determination of Total Carbon Dioxide :—For this determination, use the precipitate produced by calcium chloride at the spring. If sufficient time has elapsed between the precipitation and the examination in the laboratory, to allow the originally amorphous precipitate to crystallize, the water may be filtered at once; otherwise the flask should be warmed for some time on the water-bath. In the latter case, the stopper should be put in lightly, to avoid the generation of pressure and possible breaking of the flask.

Rinse the precipitate into a flask, and determine the carbon dioxide as given on page 54.

Since a measured volume of the water was taken for the precipitation at the spring, the specific gravity of the water must be considered in the calculation. To find the weight of the water, it is only necessary to multiply the volume taken by the specific gravity.

Direct Determination of Free and Combined Carbon Dioxide:—W. Borchers* has recommended the use of the author's apparatus shown in Fig. 19, for the direct determination of free and combined carbon dioxide. Instead of the decomposing flask shown in the figure, Borchers uses an Erlenmeyer flask of 500–600 cc. capacity; the flask should be provided with a 300 cc. mark. To avoid a loss of carbon dioxide while taking a sample from the bottle filled at the spring, close the bottle with a 2-hole rubber stopper, through which passes two glass tubes, one of the tubes is drawn out to a point and bent up in the form of a hook, and reaches to the bottom of the flask, and the other is bent at a right angle just below the stopper. Before removing the stopper put in at the spring, the flask of water should be cooled in ice water. By inverting the bottle, the sample of 300 cc. may now be transferred to the decomposing flask with a minimum loss of carbon dioxide.

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* Jour. f. prakt. Chem., Vol. 17, p. 353.

It is advisable to substitute a Liebig absorption bulb, or other similar apparatus filled with potassium hydroxide, for the soda lime tube, immediately behind the tube filled with sulphuric acid, so as to be able to tell when the decomposition is complete. Connect the potash bulb with a U-tube filled with soda-lime.

Transfer 300 cc. of the water from the bottle to the decomposing flask, connect at once with the remainder of the apparatus and slowly heat to boiling; continue the boiling until the potassium hydroxide in the Liebig bulb begins to suck back. Now aspirate about 1 liter of air freed from carbon dioxide, through the apparatus, while still boiling; cease aspirating air, and again boil until the potassium hydroxide again begins to suck back. If the water contains much bicarbonate, the above treatment must be repeated several times, since the bicarbonate decomposes but slowly into the normal carbonate. Reweigh the Liebig bulb and the soda-lime tube. The increase in weight is due to free carbon dioxide and one-half the carbon dioxide of the bicarbonates.

To determine the combined carbon dioxide, again connect the absorption apparatus with the train, and liberate the carbon dioxide with hydrochloric acid. Proceed as given in the Determination of Carbon Dioxide in Carbonates, page 54.

Determination of Total Solids:—Weigh one of the filled bottles, and evaporate the contents in a weighed platinum dish on the water-bath; if the water contains a large quantity of dissolved gas, care must be taken not to heat too rapidly at first, otherwise effervescence may cause a loss. After each addition of water from the bottle, the dish should be covered with a watch glass. Rinse out the bottle several times with distilled water, and weigh again. Dry the residue in the dish, in an oil-bath at 160° C., to constant weight.

If the weighed residue is changed to sulphates by treating with dilute sulphuric acid and igniting with ammonium carbonate, the weight may be used as a check on the other determinations of the analysis. That is to say, the weight of sulphates, minus the ferric oxide, silica and and phosphoric acid found, should agree with the sum of the weights of the metals with the exception of iron, calculated as sulphates.

Determination of Sulphuric Acid :—For this determination, use the contents of one or several bottles, according to the amount of sulphuric acid present, as shown by qualitative tests. Concentrate the water by evaporation, acidify with hydrochloric acid and precipitate with barium chloride as usual. For the determination of sulphuric acid in water containing hydrogen sulphide, see page 335.

Determination of Chlorine:—This determination is given in detail on page 321. If the water contains bromine or iodine, it will be found in the silver precipitate and must be subtracted from the latter to obtain the correct weight of chlorine.

Hydrogen sulphide water should previously be warmed with ammoniacal hydrogen peroxide, to decompose the sulphides.

Determination of Bromine, Iodine, Flourine, and Boron :—As these constituents are generally present in but small amounts, and as a large amount of water must be evaporated, it is convenient to determine them in the same portion of water.

Evaporate the contents of one of the large carboys, taking care that the water remains alkaline in reaction during evaporation; add sodium carbonate, if necessary. This precaution will not be necessary if the water belongs to the class known as alkaline mineral waters. Digest the residue several times with large quantities of distilled water, and rinse the insoluble portion onto a filter. The insoluble portion may contain the carbonates and sulphates of calcium, barium, strontium and magnesium, together with iron and manganese compounds, silica, and all the fluorine in the form of calcium fluoride. Treat the residue on the filter with dilute hydrochloric acid, and fuse the residue, consisting of sulphates of the earths, calcium fluoride and silica, in a platinum crucible with sodium carbonate. The aqueous extract of the fuse contains sodium silicate and sodium fluoride, while barium, strontium, etc., remains insoluble in the form of carbonates. To separate silica, and determine fluorine as calcium fluoride, proceed as given under Phosphorite.

Divide the solution obtained by extracting the residue, (filtrate from the carbonates and sulphates of the alkaline earths) into three weighed portions for the determination of boron, iodine and bromine. To determine boric acid, acidify one portion with hydrochloric acid, add about 1 gram of magnesium chloride and some ammonium chloride and then supersaturate with ammonium carbonate. Evaporate the solution to dryness in a platinum dish, maintaining alkaline reaction by adding ammonium hydroxide from time to time; ignite the residue of magnesium borate, magnesium chloride and magnesium hydroxide. Extract the ignited residue several times with hot water, and again evaporate the filtrate to dryness with magnesium chloride, ammonium chloride and ammonium hydroxide to obtain the last traces of the boric acid. Extract this residue with hot water, add to the first residue, transfer to a weighed platinum crucible, evaporate with water several times, and finally ignite and weigh.

Test a small portion of the weighed residue for boric acid, by moistening a platinum wire with concentrated sulphuric acid, adding a small portion of the residue and trying the flame reaction. If boric acid is present, divide the weighed residue into 2 unequal parts. Dissolve the larger portion in cold nitric acid and precipitate the silver as silver chloride, and the magnesium as phosphate from the hydrochloric acid solution of the smaller portion (Bunsen). See page 27.

If A represents the weight of the mixture of magnesium borate, magnesium chloride and magnesium oxide, B the weight of the silver chloride found by analysis, C the weight of the magnesium pyrophosphate found by analysis, and x the amount of boric acid, then,

$$x = A - \frac{\mathrm{Cl} - \mathrm{O}}{\mathrm{AgCl}} . B - \frac{2\mathrm{MgO}}{\mathrm{Mg_2P_2O_7}} . C$$

$$\text{or, } x = A - 0.19142 \,.\, B - 0.36037 \,.\, C.$$

To determine the iodine, use a second portion of the water. Various methods have been suggested for this determination. If there is considerable iodine present, precipitate it as palladous iodide, $\mathrm{PdI_2}$. Acidify slightly with nitric acid and proceed as given on page 44.

If but a trace of iodine is present, the following method is more suitable. Acidify the water slightly with hydrochloric acid and precipitate the iodine by a few drops of a solution of nitrogen peroxide in sulphuric acid, or by fuming nitric acid, and shake out the iodine with carbon bisulphide in a separatory funnel.

When the carbon bisulphide has taken up all the iodine, draw it off, wash, and titrate with a very dilute solution of sodium thiosulphate solution, shaking after each addition. The sodium thiosulphate solution should be standardized in a similar manner by adding a few cubic centimeters of iodine solution of known strength (about N/100) to carbon bisulphide, shaking out as given above, and then titrating. See Volumetric Analysis.

Bunsen used chlorine water of known strength for the separation and determination of iodine. To determine small quantities of iodine, chlorine water saturated at the ordinary temperature should be diluted with 20 times its volume of water, and for larger quantities of iodine, with twice its volume of water. The strength of this solution may be ascertained as follows: Take a measured volume (100–150 cc. of the dilute, and about 40 cc. of the concentrated), add to a solution of potassium iodide, and determine the liberated iodine with sodium thiosulphate. See page 118.

Acidify the water with hydrochloric acid and then add sufficient chloroform so that a few cc. remain undissolved after shaking in a separatory funnel. Now add the chlorine water, drop by drop, shaking the funnel after each addition. Continue the addition of chlorine water until the violet color of the chloroform has just disappeared, or the yellow color due to the liberated bromine, just appears.

If the iodine has been precipitated as palladous iodide with palladous nitrate, the filtrate may be used for the determination of bromine. It is necessary, however, to first completely remove the chlorine. Add sodium carbonate to alkaline reaction, evaporate to dryness on the water-bath and extract the residue repeatedly with warm, absolute alcohol.

The alcoholic solution contains all the bromine in the form of potassium or sodium bromide, together with a small amount of alkaline chloride. Add a few drops of sodium hydroxide, remove the alcohol by evaporation, acidify with nitric acid and precipitate the bromine and chlorine with silver nitrate. The bromine may now be determined from the loss in weight after the bromine has been replaced by chlorine. See page 46.

Instead of replacing the bromine by chlorine, the weighed precipitate may be reduced by the electric current, and the metallic silver then weighed. For this purpose, place a small piece of platinum foil connected with a platinum wire, on the precipitate, partly fill the crucible with dilute sulphuric acid and hang a second platinum foil in the acid, for a positive electrode. Connect the two poles to a suitable source of current, and the silver precipitate will soon be reduced. The end of the reduction is shown by the bottom of the crucible being covered with nothing but porous metallic silver. Decant off the liquid, wash the silver by decantation, ignite gently and weigh.

Bromine and iodine may be determined in a similar manner, if the iodine has previously been separated by nitrogen peroxide and sulphuric acid, without the use of nitric acid. Extract the iodine with carbon bisulphide, and the bromine is then in the layer above the carbon bisulphide. The bromine can now be determined as given above. Bunsen also used a solution of chlorine for the determination of bromine. Nearly neutralize the third portion of water with hydrochloric acid, concentrate in a white porcelain dish until the salts begin to crystallize out.

Boil, and add chlorine water, drop by drop, from a burette held close to the surface of the liquid. Bromine and iodine are liberated and color the liquid yellow. By boiling the solution, the bromine and iodine may be completely volatilized. When the liquid is colorless, add more chlorine, and boil again; continue in this manner until the color does not return on adding a drop of chlorine water.

The amount of bromine is found by subtracting the number of cubic centimeters of chlorine water corresponding to the iodine, from the number of cubic centimeters of chlorine water required by both bromine and iodine, and calculating the difference to bromine.

If the original water is colored by organic matter, add sodium hydroxide and evaporate to dryness in a platinum dish; transfer to a silver crucible and ignite.

Determination of Nitric Acid:—Nitric acid may be determined as given on page 323.

The determination of nitric acid may also be combined with the determination of ammonia. In the latter case, the solution in the retort, after expelling the ammonia, is used for the determination of nitric acid. The nitric acid is reduced to ammonia by warming with zinc and the excess of sodium hydroxide used to expel the ammonia:

$$KNO_3+7NaOH+4Zn=(3ZnNa_2O_2+ZnNaKO_2)+2H_2O \\ +NH_3.$$

Now concentrate the contents of the retort by evaporation, add zinc powder and pass the ammonia and hydrogen into a dilute solution of hydrochloric acid. See page 109.

Instead of zinc powder, Bunsen used 4 or 5 spirals made by twisting iron and zinc wire together and then winding them around a glass rod.

After standing for 12 hours, heat the contents of the retort on the water-bath until no more evolution of gas takes place. Add distilled water to the retort and boil over a free flame until half the contents has distilled over.

As mentioned on page 110, the ammonia may be passed into a measured quantity of standard oxalic acid (about N/100), and the excess titrated back with a standard alkali. See: Volumetric Analysis: Alkalimetry.

If, in the latter case,
t, represents the number cc. of oxalic acid taken,
a, the weight of acid ($H_2C_2O_4+2H_2O$) in one cc., and
t′ the number cc. of unneutralized acid,
then, the sample of water taken contains,

$$\frac{N_2O_5}{H_2C_2O_4+2H_2O}a\ (t-t')\ \text{grams of nitric acid.}$$

Determination of Ammonia:—Use about 1000–2000 grams of the water. Add hydrochloric acid and concentrate to a small volume in a porcelain dish. Proceed as given on page 109.

Determination of Calcium, Strontium, Barium, Magnesium, Iron, Manganese, Aluminum, Phosphoric Acid, Silica and Organic Matter:—Acidify about 5000 grams* of the water with hydrochloric acid and evaporate to dryness in a platinum dish, with the precautions given under Determination of Total Residue. As the water on long standing may precipitate calcium carbonate and ferric hydroxide, the flask should be rinsed out with dilute hydrochloric acid and then with water.

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* The amount of water to be taken depends upon the amount of mineral matter in the water.

Heat the residue at 120° C. to dehydrate the silicic acid, moisten with hydrochloric acid, warm on the water-bath and dilute with a little water. Filter out the silica, wash, ignite and weigh. If the silica is colored by organic matter, extract it with alcohol and ether before igniting. Evaporate off the ether and alcohol, and weigh the organic matter.*

The silica should be tested for purity with hydrofluoric acid or ammonium fluoride ; if there is a residue of barium or strontium sulphate, or titanic acid, dissolve it and add the solution to the main solution.

Heat the filtrate from the silica to boiling in a platinum dish, add a few drops of nitric acid, and precipitate the aluminum, iron and phosphoric acid with ammonium hydroxide.

Wash the precipitate with hot water, dissolve in hydrochloric acid and reprecipitate with ammonium hydroxide. A small amount of silica is generally found on dissolving the first precipitate. Iron, aluminum and phosphoric acid may be separated by Berzelius' method, as follows : Fuse the precipitate in a platinum crucible with 6 times its weight of a mixture of 6 parts of sodium carbonate and 1 1/2 parts of silica, and digest the fuse with hot water. The aqueous solution contains all the phosphoric acid in the form of sodium phosphate, together with the excess of sodium carbonate and silica. To separate the silica, warm the solution, add ammonium carbonate, allow to stand in a warm place and then filter; acidify the filtrate with hydrochloric acid and evaporate to dryness in a platinum dish to separate the remainder of the silica. The phosphoric acid is now precipitated with magnesia mixture as usual.

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* For the determination of organic matter by igniting the total residue, see note on p. 330.

Dissolve the insoluble residue from the fuse in hydrochloric acid and evaporate to dryness to separate the small amount of silica present. Precipitate the iron with an excess of pure potassium hydroxide, and proceed as given on page 123.

Transfer the filtrate from the original ammonium hydroxide precipitate to a beaker of suitable size, and precipitate the manganese with a slight excess of ammonium sulphide. To prevent the calcium being precipitated, fill the flask with boiled water, and stopper. The precipitate of manganous sulphide may still contain some calcium carbonate. Dissolve it in acetic acid (which leaves zinc, cobalt and nickel sulphides undissolved) and repeat the precipitation. Unite the filtrates.

Acidify the filtrate from the manganous sulphide with hydrochloric acid, and warm until the odor of hydrogen sulphide is gone. Filter off the sulphur, neutralize the filtrate with ammonium hydroxide and then add ammonium oxalate in slight excess. When the calcium oxalate has settled, filter it out, wash 2 or 3 times, dissolve in hydrochloric acid and reprecipitate. Ignite to calcium oxide and weigh.

If the water contains barium and strontium, they will be precipitated with the calcium. The calcium oxalate may also contain a small amount of magnesium. To determine these constituents, heat the weighed precipitate in the platinum crucible with nitric acid until a clear solution is obtained, and then evaporate to dryness. The residue consists of nitrates of calcium, barium, etc. Warm the residue with a very small amount of absolute alcohol, allow to stand for 24 hours, and then filter off the insoluble nitrates of barium and strontium; the filtrate contains calcium and magnesium nitrates. Evaporate the alcoholic filtrate to dryness, dissolve in hydrochloric acid and evaporate again to dryness. Dissolve in water and precipitate the calcium as oxalate. Evaporate the filtrate from the calcium to dryness, volatilize the ammonium salts by gentle ignition, dissolve in dilute hydrochloric acid and precipitate the magnesium as given on page 27.

Dissolve the barium and strontium nitrates in hot water, evaporate to dryness in a weighed platinum dish and dry at 140° C., to constant weight. To separate the barium and strontium, ignite the nitrates strongly over the blast lamp to form oxides and then dissolve in hydrochloric acid.

Evaporate to dryness and treat the residue with absolute alcohol, which dissolves strontium chloride and leaves barium chloride insoluble. Filter out the insoluble barium chloride and wash with absolute alcohol. Dissolve the barium chloride off the filter with hot water and evaporate to dryness with a few drops of sulphuric acid, in a weighed platinum crucible.

The strontium chloride in the alcoholic filtrate is likewise precipitated as sulphate, after the alcohol has been removed by evaporation.

The filtrate from the calcium oxalate contains the magnesium, together with a small amount of calcium. Evaporate to dryness in a platinum dish, volatilize the ammonium salts by gentle ignition and dissolve the residue in dilute hydrochloric acid. Precipitate the magnesium as ammonium-magnesium phosphate, as given on page 27. To recover the calcium from the magnesium pyrophosphate, dissolve the weighed precipitate in concentrated hydrochloric acid, precipitate with ammonium hydroxide and redissolve in acetic acid. From this solution, precipitate the calcium with ammonium oxalate.

Determination of Potassium and Sodium :—In the case of mineral waters containing a considerable amount of sodium chloride, the contents of 1 or 2 bottles will be sufficient for the analysis.

Concentrate the water by evaporation in a porcelain dish, boil, and precipitate with an excess of baryta water. Filter, and evaporate the filtrate to dryness in a platinum dish. Dissolve the residue in the least amount of water necessary, filter, if necessary, and precipitate with ammonium hydroxide and ammonium carbonate ; evaporate the filtrate from the barium carbonate to dryness in a platinum dish, volatilize the ammonium salts by gentle ignition, dissolve in water and add more ammonium carbonate. Filter, if a precipitate is formed, and test again to be sure that all non-alkaline bases are removed. When all the non-alkaline bases are removed, evaporate to dryness in a platinum dish, and volatilize the ammonium salts by gentle ignition. Dissolve the salts in water, and digest for 2 hours with freshly precipitated mercuric oxide, to remove the last traces of magnesia. Filter, evaporate to dryness in a platinum dish and gently ignite to expel the slight amount of mercuric oxide. Dissolve the residue in a little water, filter into a weighed platinum dish, acidify with hydrochloric acid and evaporate to dryness. Ignite below a very dull red heat, and weigh as

$KCl + NaCl$. Separate the potassium and sodium as given on page 103.

The alkaline chlorides always contain a small amount of magnesium chloride; they also contain lithium, if the latter element is contained in the water.

To determine the magnesium in the precipitate, evaporate the filtrate from the potassium-platinic chloride, on the water-bath, to expel the alcohol, and rinse into a long-necked flask, connect with a hydrogen generator and warm; this reduces the sodium-platinic chloride and the excess of platinic chloride to metallic platinum. As soon as the solution has become colorless, filter out the platinum and precipitate the magnesium in the filtrate, as usual.* Calculate the magnesium pyrophosphate to magnesium chloride, and subtract the weight from the weight of the mixed chlorides. (Laspeyres.)

The calcium and magnesium may also be separated as oxalates, and the alkalies determined in the filtrate.

Determination of Lithium, and Detection of Caesium and Rubidium:—As a general rule, mineral waters contain but a small amount of lithium compounds, so that for its determination a large amount of water must be evaporated. If a considerable amount of water was used for the determination of potassium and sodium, lithium may be determined at the same time. Evaporate the filtrate from the metallic platinum to dryness, extract the residue of sodium chloride and lithium chloride with ether-alcohol, and proceed as given below.

If a special quantity of water was used for the lithium determination, qualitative tests for caesium and rubidium may be made on the same residue. Separate barium, strontium, calcium, iron, manganese, etc., as given in the determination of bromine, iodine, fluorine and boron, page 341. Add sodium carbonate to the clear solution and evaporate to dryness. Extract the residue with water, concentrate the filtrate, slightly acidify with hydrochloric acid and precipitate in the cold with platinic chloride. The precipitate contains potassium-platinic chloride, together with caesium and rubidium platinic chlorides, while lithium and sodium-platinic chlorides remain in solution. The detection of rubidium and caesium, in the presence of potassium, depends upon the easy solubility of potassium-platinic chloride in water. After standing for 24 hours, filter out the precipitate, and boil in a platinum dish 25–30 times with small portions of water; add only sufficient water to cover the precipitate. If, after cooling, a precipitate separates in the water decanted off, filter, and treat in the same manner as before; unite the 2 residues, and test for caesium and rubidium with the spectroscope.

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* It is simpler to separate the platinum electrotytically. See: foot note, p. 1.

Determination of Lithium:—Reduce the platinum salts in solution with hydrogen, and boil the filtrate from the platinum with baryta water to remove barium, strontium, etc. Separate the excess of barium and a trace of calcium with ammonium hydroxide and ammonia carbonate, filter, evaporate the filtrate to dryness in a platinum dish and volatilize the ammonia salts by gentle ignition.

Dissolve the salts in water, filter, if necessary, and acidify with hydrochloric acid. In the case of mineral waters rich in sodium chloride, it is desirable to remove the latter as much as possible before extracting with ether-alcohol. Concentrate the acidified solution by evaporation, filter out the crystallized sodium chloride, wash several times with cold water and repeat the operation. (Bunsen). Finally evaporate to dryness on the water-bath, heat with a free flame to remove moisture, and then repeatedly extract the mixture with ether-alcohol. Repeat these operations until a small portion of the filtrate does not give the lithium flame coloration. Then evaporate the alcoholic extract on the water-bath, dissolve the residue in water and test with ammonium carbonate, to see if calcium is still present. If the latter is present, the filtrate must be evaporated to dryness, the residue ignited and again dissolved in water and tested for calcium. Finally evaporate to dryness, dissolve in dilute hydrochloric acid, again evaporate to dryness and volatilize the ammonium salts. Extract the residue with ether-alcohol. Filter out the small amount of sodium chloride and determine the lithium in the filtrate, as given on page 138.

Qualitative Detection of Copper, Bismuth, Lead, Arsenic, Antimony, Tin, Cobalt, Nickel, Zinc, Barium, Strontium and Titanium:—These substances are contained in mineral waters in such small amounts that in most cases even very large quantities of the water scarcely suffice for their detection. For this purpose, however, the deposits collected at the spring are suitable. These should have been rinsed free from adhering mineral water with distilled water. To detect arsenic, antimony and tin, fuse a sample of the deposit with twice its weight of a mixture of equal parts of sodium carbonate and potassium nitrate. Dissolve the fused mass in water, acidify with dilute sulphuric acid and evaporate to dryness on the water-bath. Dissolve the residue in water and saturate with hydrogen sulphide. Treat the precipitate with potassium or sodium sulphide, which dissolves the sulphides of arsenic, antimony and tin; the latter may be reprecipitated by adding a dilute acid. The individual elements may be detected, as usual.

To detect the remaining metals, dissolve another portion of the deposit in hydrochloric acid, precipitate with hydrogen sulphide and oxidize the sulphide precipitate with fuming nitric acid, to destroy the organic matter precipitated with the sulphides. Separate arsenic, antimony, and tin, by neutralizing with potassium hydroxide and digesting with sodium sulphide.

Dissolve the residual sulphides in nitric acid, and precipitate the lead with sulphuric acid. Copper and bismuth will be found in the filtrate from the lead sulphate, and may be precipitated by ammonium carbonate. The precipitate should be examined qualitatively.

The filtrate from the sulphide precipitate contains manganese, cobalt, nickel, etc.; precipitate with ammonium hydroxide and ammonium sulphide, and test qualitatively.

In the examination of deposits containing much iron, Bunsen recommends the following method for detecting cobalt and nickel: Remove the hydrogen sulphide group, expel the hydrogen sulphide, neutralize with sodium carbonate and boil with freshly precipitated manganous sulphide. Cobalt and nickel are precipitated, and may be separated from the manganous sulphide by treating with acetic acid.

Barium, Strontium and Titanium are to be sought by the usual methods, in the portion of the deposit insoluble in hydrochloric acid. The silica should be tested for titanium, as given on page 124.

ASHES.*

Constituents: Ferric Iron, Aluminum, Manganese, Calcium, Magnesium, Alkalies, Silica, Carbonic Acid, Sulphuric Acid and Hydrochloric Acid.

The ashes may be obtained by incinerating the plants, seeds, fruits, etc., in a platinum dish in a muffel, or at a low temperature over a free flame, after drying at 100° C.

The latter method is applicable in all cases, especially if the suggestion of F. Schulze is followed. Schulze recommends supporting a cylinder of glass over the dish, as shown in Fig. 53. The incineration may then be effected, even at a very low red heat, and no loss of alkalies by volatilization need be feared. After the ash has been ignited to constant weight, pulverize it and preserve it in a bottle.

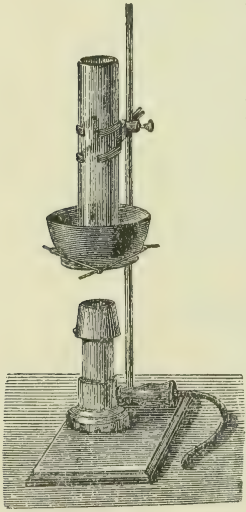

Fig. 53.

Place about 10 grams of the ash in a glass stoppered cylinder of about 300 cc. capacity, add about 20 cc. of water and replace the air by carbon dioxide. Shake the contents of the bottle vigorously, refill with carbon dioxide, and repeat the shaking until the liquid is completely saturated.

Rinse the contents of the cylinder into a dish, evaporate to dryness on the water-bath and heat the residue on some time at 160° C. If crystalline calcium carbonate has precipitated on the walls of the cylinder, and cannot be removed by shaking with water, add more water, saturate it with carbon dioxide and shake until soluble calcium bicarbonate is formed. Extract the dried insoluble matter on a filter that has been dried at 100° C. and weighed, and concentrate the filtrate by evaporation, On evaporation, calcium sulphate generally separates out; filter it in the same manner, on a weighed filter.

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* [Compare: H. W. Wiley. Bull. 46, U. S. Dept. Agricult. 1899. p. 77.]

The aqueous extract of the ash contains the alkaline carbonates and sulphates, together with chlorides and a small amount of phosphates; the residue contains the alkaline earth carbonates and phosphates, together with silica, oxide of iron, alumina and oxides of manganese.

Immediately after filtration, divide the aqueous extract of the ash into 5 weighed portions. In one portion, determine chlorine as usual.

In a second portion, determine sulphuric acid, as barium sulphate, after acidifying with hydrochloric acid.

To determine the alkalies, precipitate one of the weighed portions by boiling with baryta water; proceed as given on page 351.

Acidify the fourth portion with hydrochloric acid, and boil to decompose the carbonates. Add ammonium hydroxide to alkaline reaction, and then dissolve the resulting precipitate in acetic acid. From this solution, precipitate the small amount of calcium with ammonium oxalate. Filter, and precipitate the remainder of the phosphoric acid with magnesium chloride, from the ammoniacal solution.

If no phosphoric acid is present, separate calcium and magnesium in the usual manner.

The carbon dioxide may be determined in the fifth portion, either by direct weighing, or by loss on ignition of the residue after evaporation.

Analysis of the weighed Insoluble Residue:—Intimately mix the residue in an agate mortar, treat about 2 grams with nitric acid containing nitrous acid* and digest on the water-bath to complete solution. Evaporate to dryness, dissolve the residue in nitric acid and water, and filter off the silica. Dilute the filtrate to a definite volume, and determine the phosphoric acid in an aliquot part.

Expel the excess of acid in another portion, or in the entire remainder, by evaporation, add a sufficient amount of lead acetate to precipitate the phosphoric acid, filter, and remove the excess of lead with hydrogen sulphide. After filtering out the lead sulphide, boil off the excess of hydrogen sulphide, oxidize the ferrous iron, boil, and precipitate the iron and alumina with ammonium hydroxide. It is advisable to dissolve the washed precipitate in hydrochloric acid and repeat the precipitation. Ferric oxide and alumina may be separated by the usual methods. If the phosphoric acid was precipitated by lead acetate in a too strongly acid solution, the precipitate of ferric oxide and alumina will be contaminated with phosphoric acid.

Precipitate the manganese in the filtrate with a few drops of ammonium sulphide. After destroying the excess of the latter in the filtrate, with hydrochloric acid, precipitate calcium and magnesium as usual.

Instead of determining the phosphoric acid and the metals in separate portions, the method of Reissig may be used. Add 2–3 grams of pure metallic tin to the solution, add fuming nitric acid and digest until no more oxidation takes place.

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* The nitrous acid is used to effect the solution of the oxides of manganese.

When the precipitate of stannic oxide and stannic phosphate has completely settled, filter, and wash with water. Digest the precipitate in a platinum dish with a very little concentrated potassium hydroxide.* Dilute the alkaline liquid, which contains potassium phosphate and potassium stannate, with 900 cc. of water, in a weighed liter flask, and saturate with hydrogen sulphide. If a precipitate of ferrous sulphide separates, filter it out, return the filtrate to the weighed flask, add dilute sulphuric acid to acid reaction, fill to the mark with water, and weigh. After the stannic sulphide has completely settled, which requires 10–12 hours, filter about 2/3 of the clear, supernatant liquid through a dry filter into a weighed flask, and weigh again. Use the weighed filtrate for the determination of phosphoric acid. Concentrate by evaporation, neutralize with ammonium hydroxide and precipitate with magnesium chloride.

To ascertain what proportion of the entire solution was used for the determination of the phosphoric acid, it is only necessary to subtract the weight of stannic sulphide corresponding to the weight of tin taken, from the weight of the entire solution.

Ferric oxide, alumina, etc., are contained in the filtrate from the stannic phosphate and stannic oxide. First pass a current of hydrogen sulphide to remove the impurities contained in the tin (generally copper), boil off the hydrogen sulphide, oxidize with nitric acid, precipitate with ammonium hydroxide, etc.

Take a separate, weighed portion of the residue that was insoluble in water, for the determination of carbon dioxide, silica and sulphuric acid. The carbon dioxide may be determined by direct weighing, or it may be determined by difference. See analysis of Soda Ash. After expelling the carbon dioxide, evaporate the residue to dryness in a platinum dish and separate the silica as usual. Precipitate the sulphuric acid in the filtrate with barium chloride.

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* An excess should carefully be avoided; otherwise a precipitate may separate.

GUANO.

Determination of Water:—When guano is dried at 100–120° C., ammonia, as well as water, is volatilized. The ammonia must, therefore, be absorbed, and its weight subtracted from the total loss of weight of the sample on drying, to get the amount of moisture. Stohmann has constructed a special apparatus, Fig. 54, for this purpose.

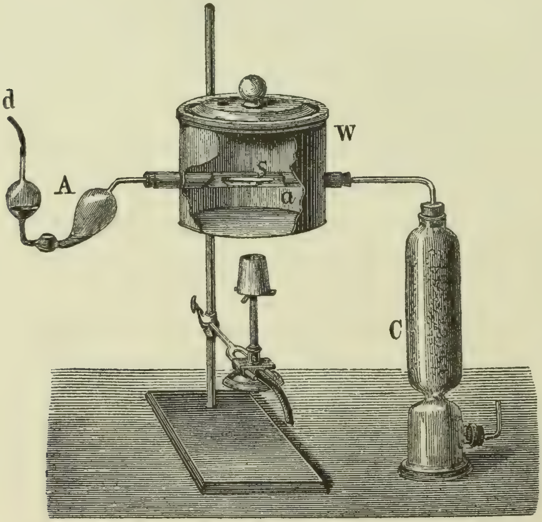

Fig. 54.

W is a water-bath, into which the brass tube a is soldered. The boat s contains the guano, a is connected on one side with the drying-tower C, filled with calcium chloride, and on the other side, with the pear-shaped bulb A, for absorbing the ammonia. The bulb A contains a measured volume of oxalic or sulphuric acid of known strength (about 10 cc. of solution containing 0.6285 gram of oxalic acid, $H_2C_2O_4+2H_2O$, or 0.4891 gram of sulphuric acid, H_2SO_4, corresponding to 0.170 gram of ammonia). Weigh a quantity (5–10 grams) of the pulverized guano in the boat s, shove the boat into the tube a, connect the latter with C and A and heat the water in W to boiling; at the same time aspirate a slow current of air through the apparatus. When the contents of the boat have come to constant weight, titrate the excess of acid with standard sodium hydroxide or ammonium hydroxide, and subtract the weight of ammonia from the loss of weight of the boat.

Determination of the Total Non-Volatile (fixed) Constituents :—Proceed exactly as described in the analysis of Ashes, page 356, heating the residue from the water determination in a platinum dish at a very low temperature, until the weight becomes constant. If alkaline earth carbonates are present, they may lose more or less of their carbon dioxide, according to the temperature. It is therefore necessary to moisten the ignited residue with ammonium carbonate, ignite gently, and weigh. The resulting ash should be kept in a well-closed bottle for the future determination of single constituents.

Determination of the Individual Non-Volatile Constituents :—Usually, the determination of phosphoric acid, sulphuric acid, calcium, and alkalies is all that is necessary. As regards the phosphoric acid, it has heretofore been estimated by digesting a weighed sample with nitric acid, and determining the phosphoric acid in the solution, either gravimetrically or volumetrically.

Gilbert found that, upon digesting the ash with nitric acid, the pyrophosphate that had been formed by ignition, was not fully changed into the ordinary phosphate and consequently the acid existing in the residue as calcium pyrophosphate was not included in the estimation. The conversion succeeds, however, readily and perfectly if the incinerated guano is fused in a platinum crucible with 4 times its weight of a mixture consisting of 2 parts sodium carbonate and 1 part potassium chlorate.*

Ignite at a low red heat until the contents of the crucible become white, then heat for a quarter of an hour at a full red heat. Pour the contents of the crucible into a platinum dish, digest for some time with water on the water-bath, and then add nitric acid to acid reaction. If the guano contains silica, evaporate to dryness, moisten with nitric acid and water, and separate as usual. The phosphoric acid may be determined in the filtrate, either gravimetrically or volumetrically. The details of the gravimetric method are given on page 41.

To convert the nitric acid solution into an acetic acid solution for the purpose of determining the phosphoric acid volumetrically, dissolve the precipitate produced by sodium hydroxide in the least possible quantity of acetic acid. When iron and aluminum are present, their phosphates, $FePO_4$ and $AlPO_4$, will remain insoluble in acetic acid. If the precipitate is pure iron or aluminum phosphate, filter it out, wash with hot water, ignite and weigh. Calculate the phosphoric acid contained in the precipitate. If, however, the precipitate is a mixture of the two compounds, and they are in considerable quantity, to make an accurate determination, the phosphoric acid must be separated from the bases, as given on page 159.

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* Potassium nitrate may be used instead of potassium chlorate. The former is preferable in the analysis of products which contain difficulty combustible, nitrogenous matter.

To determine sulphuric acid, digest a second portion of the ash repeatedly with nitric acid, and evaporate to dryness on the water-bath ; dissolve the residue in dilute hydrochloric acid, filter, and precipitate the sulphuric acid in the filtrate with barium chloride.

The calcium is most advantageously determined in the nitric acid solution of a third portion of the ash, by evaporating it to dryness with sulphuric acid, forming calcium sulphate. See page 101.

Remove the nitric acid as much as possible from the solution of a fourth portion of the ash, and boil the solution with baryta water to precipitate the non-alkaline bases ; filter, remove the calcium and magnesium with ammonium carbonate, and determine the alkalies as given on page 351.

In the complete analysis of the fixed residue, all the constituents, with the exception of the alkalies, may be determined in the same portion. Fuse the sample with sodium carbonate and potassium chlorate, as given above, filter out the silica, and dilute the filtrate to a definite volume. If calcium sulphate is present in appreciable quantity, the silica will retain a slight amount of it. In such a case, it is necessary to digest the silica several times with small amounts of dilute nitric acid.

Determine phosphoric acid and sulphuric acid in measured portions of the solution. The barium sulphate should be extracted several times with hot water before transferring to the filter, and it should also be extracted with dilute hydrochloric acid after ignition.

To determine the remaining constituents, separate the phosphoric acid with tin in a separate portion of the solution, and proceed as given on page 149.

Determination of Constituents Soluble in Water, and of those Insoluble in Water:—For the determination of these constituents, use about 10 grams of the un-dried guano. Place the sample in a flask, add about 200 cc. of water, shake a few times and filter at once on a filter that has been dried at 100° C. and weighed. Wash the insoluble residue with small quantities of water, using the suction pump, and dry at 100° C., to constant weight. By incinerating the residue, the fixed constituents may be obtained. The quantity of matter soluble in water, is obtained by difference. If the entire quantity, or a portion of the non-volatile constituents, is to be determined in the aqueous solution, evaporate the solution to dryness in a platinum dish and ignite. The estimation of the individual constituents, soluble or insoluble in water, is executed as given above.

Determination of Carbon Dioxide:—Many guanos contain carbonates in greater or less quantities; in this case, the carbon dioxide may be estimated as given above.

Determination of Total Carbon:—Use a portion of the substance that has previously been dried at 100° C., and determine the carbon either by ignition in a current of oxygen, as given under Organic Analysis, or by oxidation with chromic acid and sulphuric acid, as given on page 303. As oxides of nitrogen are formed when nitrogenous organic matter is ignited with copper oxide, a roll of copper gauze should be placed in the end of the combustion tube, next to the absorption apparatus. In employing the first method, it is further necessary, as the ash constituents readily contain carbon dioxide, to mix the guano before combustion, with boric oxide, antimony oxide or copper phosphate, which will completely expel the carbon dioxide. If a mixture of 9 parts of lead chromate and 1 part of potassium bichromate, is used instead of copper oxide for the oxidation of the organic matter, the carbon dioxide is completely evolved without the other agents; the oxides of nitrogen, however, are more readily formed.

Determination of Nitric Acid ;—Extract a weighed portion of the fertilizer with cold water, add sodium carbonate to the extract to alkaline reaction, allow to stand some time, and then filter. Determine the nitric acid in a portion of the filtrate, as given on page 323, or 346. When using the method subsequently described for the determination of ammonia, (by boiling with magnesia), the nitric acid determination can be made at the same time. Proceed as given on 367.

Determination of Hydrochloric Acid :—Extract a new portion of the un-dried guano with very dilute nitric acid at a low temperature, filter, and determine the hydrochloric acid in the filtrate.

Determination of Oxalic Acid :—The method is based upon the same principle as the valuation of Pyrolusite ; 2 molecules of carbon dioxide correspond to 1 molecule of oxalic acid, $H_2C_2O_4$. Mix the guano with an excess of pure manganese dioxide and add a moderate excess of sulphuric acid. The results are far more accurate if the carben dioxide is not determined by loss of weight, but by direct weighing, as given on page 56. If the guano contains carbonates, add sulphuric acid before adding the manganese dioxide, expel the carbon dioxide by warming the solution, neutralize the acid with sodium hydroxide free from carbonate, and then proceed as given above.

Determination of Uric Acid:—The uric acid is readily soluble on gently warming the guano with sodium hydroxide. Concentrate the filtrate by evaporation and acidify with dilute hydrochloric acid. After standing 24 hours, filter the separated uric acid on a filter that has been dried at 100° C. and weighed, wash with a small quantity of water, using suction, and dry to constant weight at 100° C.

Determination of Total Nitrogen:—For the method of determining nitrogen by formation of ammonia, see Organic Analysis.

Determination of Nitrogen by Kjeldahl's Method*:—The method is based upon the fact that on heating nitrogenous substances with an excess of sulphuric acid and potassium permanganate, all the nitrogen is changed to ammonia. Place the substance in a narrow-necked flask of about 100 cc. capacity, and add an excess of concentrated sulphuric acid and a small amount of phosphorus pentoxide Incline the flask at an angle and heat the contents to boiling, and boil for about 2 hours. Oxidize the hot solution with potassium permanganate, adding the dry salt in small portions. The dark colored solution clears up and finally becomes bluish green. The appearance of the latter tint may be taken as evidence of complete oxidation. Digest the contents of the flask for 5 to 10 minutes at a gentle heat, cool, dilute with water, and determine the ammonia as given on page 109. To prevent the liquid bumping during distillation, add a few pieces of zinc before adding the potassium hydroxide.

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* Zeit. f. anal. Chem., Vol. 22, p. 366.

Determination of Total Ammonia:—The total ammonia cannot be determined by distilling a weighed quantity with potassium hydroxide, as the guano contains proteine substances which evolve ammonia when treated with potassium hydroxide.

The latter decomposition, however, does not take place if the potassium hydroxide is replaced by calcium hydroxide, (milk of lime), or by calcined magnesia. As regards the employment of calcium hydroxide, Schloesing, who proposed this method, found that the expulsion of the ammonia was complete only when the calcium hydroxide was allowed to act upon the substance for some time in the cold. The decomposition should be effected either in a tightly closed dessicator, or under an inverted beaker sealed with mercury. Dilute hydrochloric, oxalic, or sulphuric acid, of known strength, is used to absorb the ammonia, and the vessel containing the acid is supported with the aid of a glass tripod or triangle, directly over the dish containing the guano and calcium hydroxide. To prevent loss of ammonia, it is advisable to make every preparation for the absorption of the ammonia, before adding the calcium hydroxide. After standing for 48 hours, the decomposition is complete. One may easily be assured of this by introducing a piece of moist red litmus paper under the jar, when its color should remain unchanged. When using calcined magnesia (Boussingault's method) to effect the decomposition of ammonium compounds in guano, it is necessary to boil the mixture, as given in the determination of ammonia by boiling with potassium hydroxide.

SUPERPHOSPHATES*.

Superphosphates contain not only undecomposed Calcium Phosphate, but also varying amounts of Calcium Sulphate, Calcium Chloride, Phosphate of Iron, Free Phosphoric Acid, Water, and generally, Sand, Carbon, and Nitrogenous Organic Matter.

In most cases, the valuation of these products consists in the estimation of the soluble—the so-called reverted†—phosphoric acid, and the insoluble phosphoric acid.

For the complete analysis of superphosphates, proceed exactly as given in the preceding examples. First determine the water by drying a sample at 160–180° C., to constant weight.

The constituents soluble and insoluble in water, may be determined by grinding about 10 grams of the un-dried substance in a porcelain mortar with cold distilled water until the mass is finely divided. Filter, using suction, and wash the residue until the washings do not show an acid reaction. Reserve the residue for further investigation. Dilute the filtrate to a definite volume (500 cc.), and use 4 measured or weighed portions for the determination of organic matter and alkalies, sulphuric acid, hydrochloric acid, phosphoric acid and the alkaline earths.

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* On the analysis of Superphosphates, compare: Mohr—Classen, Titrirmethode, 7th edition.

† The amount of soluble phosphoric acid in the superphosphate gradually diminishes. The process of changing to the insoluble form is called "reversion." The following reaction takes place:

$$Ca_3(PO_4)_2 + CaH_4(PO_4)_2 = 4CaHPO_4.$$

According to Post, the reversion consists in the free phosphoric acid entering into reaction with the ferric oxide and alumina, and also with undecomposed tribasic calcium phosphate. There is thus formed, citrate-soluble ferric phosphate and aluminum phosphate, as well as water-soluble calcium phosphate. As the free phosphoric acid decreases, the phosphates of iron, aluminum and calcium separate from the phosphates which are soluble in water.

To determine the organic matter and alkalies, evaporate the first portion to dryness in a platinum dish, add baryta water to alkaline reaction, and evaporate to dryness. Dry at 180° C. and weigh. Ignite the residue, and treat as given on page 361. The loss of weight on ignition gives the amount of organic matter. Boil the ignited residue again with baryta water to separate calcium, magnesium, etc., filter, and determine the alkalies in the filtrate, as given on page 351.

Determine sulphuric and hydrochloric acid, as usual, in the second and third portions. If the aqueous extract is strongly colored by dissolved organic matter, the latter must be destroyed before hydrochloric acid can be determined. Add sodium carbonate and potassium nitrate to the solution and evaporate to dryness in a platinum dish. Fuse the residue, dissolve in water, and determine the hydrochloric acid in the filtrate.

Phosphoric acid and the alkaline earths may be determined in the same (fourth) portion. Add sodium carbonate to the solution and evaporate to dryness, Fuse the salts with a mixture of sodium carbonate and potassium chlorate, as given on page 361. Dissolve the fuse in dilute nitric acid, make alkaline with sodium hydroxide and then acidify with acetic acid.* Dilute the solution to a definite volume, and determine the phosphoric acid, either gravimetrically or volumetrically, in an aliquot portion of the solution.

Determine the calcium and magnesium, as usual, in the remainder of the solution.

The further treatment of the water-insoluble portion of the superphosphate, follows from what has been said on page 364, First determine its weight after drying to constant weight at 180° C., and then determine the organic matter by loss on ignition.

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* If a precipitate of iron or aluminum phosphate remains insoluble after acidifying with acetic acid, filter it out and determine it as given on p. 362.

Fuse the fixed constituents with sodium carbonate and potassium chlorate and proceed as given on page 353.

Determine nitrogen and ammonia as directed in the analysis of Guano.

Determination of Phosphoric Acid Soluble in Water:—The method follows from the preceding. Either of 2 methods may be used for extracting the soluble acid, digestion or washing. The first method consists in slowly pouring about 500 cc. of cold distilled water upon a quantity of the superphosphate, shaking repeatedly and filtering, after standing for 2 or 3 hours. The results of this method depend upon the duration of the digestion. It is not applicable when considerable quantities of ferric oxide and alumina are contained in the superphosphate, as the soluble iron or aluminum phosphate gradually decomposes with water, and separates as an insoluble tribasic phosphate of aluminum or iron (Ruempler). The results are consequently too low.

The washing method has already been described. (Determination of constituents, soluble and insoluble.) This method yields the most accurate results.

To determine the phosphoric acid, follow the method given on page 371, by evaporating to dryness with sodium carbonate and fusing the residue with sodium carbonate and potassium chlorate. Dissolve the fuse in dilute nitric acid, and either precipitate with ammonium molybdate or titrate with uranium acetate solution.

According to the investigations of Drewsen*, phosphoric acid may be precipitated with ammonium molybdate directly by previously boiling the solution for some time with nitric acid.

Determination of Reverted Phosphoric Acid:—For this determination, use the residue freed from soluble phosphoric acid by extraction with cold water. Fresenius found that by treating this residue with ammonium citrate, Sp. Gr. 1,09,† only the acid calcium phosphate, $CaHPO_4$, was dissolved, while the undecomposed calcium phosphate in the superphosphate, remained entirely undissolved.

Extract 2 grams of superphosphate with water, rinse the residue into a beaker with 100 cc. of ammonium citrate solution, Sp. Gr. 1.09, digest for half an hour at a temperature of 35–40° C. and then filter. Wash the insoluble residue 2 or 3 times with a mixture of equal volumes of the above citrate solution and water, and evaporate the filtrate to dryness in a platinum dish. Ignite the residue, first alone, and then with sodium carbonate and a little potassium nitrate. After cooling, pour water on the mass, acidify with nitric acid and warm to solution. Determine the phosphoric acid in solution, either gravimetrically by precipitation with ammonium molybdate, or volumetrically with uranium acetate.

The quantity of the reverted phosphoric acid may be calculated indirectly by difference.

In this case, determine the total phosphoric acid, the phosphoric acid soluble in water, and the phosphoric acid undecomposed after treatment with water, or the phosphoric acid insoluble in ammonium citrate.

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* Zeit. f. anal. chem., Vol. 20, p. 54.

† Herzfeld and Feuerlein use ammonium citrate of Sp. Gr. 1.105. Add 400 cc. of water to 300 grams of citric acid, and then add 325 grams of finely pulverized ammonium carbonate. Allow to stand for an hour, stirring occasionally, and then dilute with water to the above Sp. Gr.

If b represents the amount of reverted phosphoric acid sought, S the total phosphoric acid, a the phosphoric acid soluble in water and c the undecomposed phosphoric acid, then

$$S=a+b+c, \text{ and } b=S-(a+c).$$

BONE MEAL.

In a complete analysis, the amount of Fat and Glutinous Substance, as well as the Fixed (Mineral) Constituents, have to be determined.

The water may be determined by drying the bone meal at 125° C.

To determine the total fixed constituents, proceed as given under Guano, and ignite 5–10 grams of the un-dried powder until the ash appears white. Use the residue for the determination of the individual constituents, using the method given on page 361.

In many cases, a determination of phosphoric acid is all that is required. Fuse the residue, which need not be ignited until perfectly white, with 4 times its weight of a mixture of 2 parts sodium carbonate and 1 part potassium nitrate. Proceed as given on page 232.

Determination of Fat :—Extract a weighed sample of the un-dried powder in an extraction apparatus with anhydrous ether, distil of the latter, dry the fat at 100° C., and weigh it.

Determination of Glutinous Matter ;—This determination cannot be made directly, but the amount is found indirectly by difference between the weight of the sample and the sum of the weights of the fixed constituents, fat, carbon dioxide and water.

Nitrogen and carbon dioxide are determined by the method given under Guano.

BONE BLACK.

Bone Black is a mixture of Calcium Phosphate, Calcium Carbonate, and Carbon, and ordinarily contains small amounts of Ferric Oxide, Magnesium Oxide, Sodium Oxide, Sulphuric Acid, (Fluorine) etc.

First determine the water by drying a sample at 120° C.

Determine the carbon dioxide and the remaining constituents, in a second portion, (about 5 grams), by the method given on page 56, or 381. After expelling the carbon dioxide, filter the hydrochloric acid solution through a filter that has been dried at 120° C. and weighed; dry the residue at the same temperature to constant weight. The residue consists of carbon, together with undissolved organic matter, clay and sand. Ignite until all the carbon is burned off, leaving a residue of clay and sand; the amount of carbon and organic matter is found by difference.

The filtrate from the carbon, etc., contains calcium, magnesium, iron, alkalies, phosphoric and sulphuric acids. Determine these constituents by the methods given under Ashes.

If the bone black contains hydrochloric acid, it must be determined in a special sample. See page 365.

COAL.

Coal Analyses are divided into Proximate Analyses and Ultimate Analyses. The proximate analysis of coal includes the determination of Moisture, Volatile Combustible Matter, Fixed Carbon, Sulphur, and Ash. The Ultimate Analysis includes the determination of Carbon, Hydrogen, Nitrogen, Oxygen, Sulphur, Ash and Heating Effect.

The method to be used, depends upon the use to which the coal is to be put.

Proximate Analysis.*

[Determination of Moisture :—"Dry 1 gram of the coal in an open porcelain or platinum crucible at from 104–109° C. for 1 hour, best in a double-walled bath containing pure toluene. Cool in a dessicator and weigh covered.

"With coals high in moisture, and in all cases where accuracy is desired, determinations must be made both with the coarsely ground and with the powdered coal. When, as will usually be the case, more moisture is found in the coarsely ground than in the powdered coal, a correction must be applied to all determinations made with the latter. Thus, if 1 per cent. more of moisture is found in the coarsely ground sample, a total of 1 per cent. must be subtracted from the quantities of the other constituents as determined with the powdered sample. Or, in the form of a rule: Divide the difference in moisture by the per cent. of constituents other than moisture as found in the powdered coal, by the quotient, and subtract the resulting product from the amount of the given constituent.

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* [From the Report of the committee on Coal analysis to the American Chemical Society, Jour. Am. Chem. Soc., Vol. 21, p. 1116. W. A. Noyes, W. F. Hillebrand and C. B. Dudley, Committee.]

‘‘Thus, suppose the results of an analysis gave :

	Coarsely ground Coal.	Powdered Coal.
Moisture..............................	12.07	10.39
Volatile combustible matter........		34.25,

then the correction factor will be

$$\frac{12.07-10.39}{100-10.39}=\frac{1.68}{89.61}=0.0187,$$

and the true per cent. of volatile combustible matter will be,

$$34.25-(34.25\times0.0187)=33.61.$$

‘‘It is possible that volatile combustible matter and ash may be determined with the coarsely ground coal without serious error, but we have not enough data at our command to warrant such a recommendation.

‘‘The toluene bath is recommended for convenience, but any other bath at the proper temperature will answer equally well. Coals generally gain in weight, probably from oxidation, after 1 hour's heating, so that longer heating is not only unnecessary but undesirable.

Determination of Volatile Combustible Matter :—‘‘Place 1 gram of the fresh, un-dried powdered coal in a platinum crucible weighing 20 or 30 grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for 7 minutes. The crucible should be supported on a platinum triangle with the bottom from 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under side should remain covered with carbon. To find Volatile Combustible Matter, subtract the per cent. of moisture from the loss found here. The weight of the material left in the crucible is 'coke.'

Determination of Ash :—"Burn the portion of coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, until free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol.

"When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of ash; and, since 3 atoms of oxygen replace 4 atoms of sulphur, the weight of the ash is less than the weight of the mineral matter in the coal of by $\frac{5}{8}$ of the weight of the sulphur.

"While the error from this source is sometimes considerable, the committee does not recommend such a correction for 'proximate' analyses. When analyses are to be used as a basis for calculating the heating effect of the coal, a correction should be made. If it is desired to analize the ash, proceed a given under Ashes, page 356.

Determination of Fixed Carbon :—"This is found by subtracting the per cent. of ash from the per cent. of coke as found above. Sulphur, which passes partly into the Volatile Combustible Matter and partly into the coke, is not considered in the calculation.

Determination of Sulphur (Eschka's Method) :"Eschka's method is recommended for general use. Mix thoroughly 1 gram of the finely powdered coal* with 1 gram of magnesium oxide and .5 grams of dry sodium carbonate in a thin platinum dish having a capacity of 75–100 cc. A crucible may be used, but a dish is preferable. The magnesium oxide should be light and porous, not a heavy, compact variety.

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* With coals high in moisture a correction may be necessary on account of the loss of water in powdering the coal. (See above under moisture.)

"The dish is heated on a triangle over an alcohol lamp, held in the hand at first. *Gas must not be used*, because of the sulphur it contains. The mixture is frequently stirred with a platinum wire and the heat raised very slowly, especially with soft coals. The flame is kept in motion and barely touching the dish, at first, until strong glowing has ceased, and is then increased gradually until, in 15 minutes, the bottom of the dish is at a low red heat. When the carbon is burned, transfer the mass to a beaker and rinse the dish, using about 50 cc. of water. Add 15 cc. of saturated bromine water and boil for 5 minutes. Allow to settle, decant through a filter, boil a second and third time with 30 cc. of water, and wash till the filtrate gives but a slight opalescence with silver nitrate and nitric acid. The volume of the filtrate should be about 200 cc. Add 1.5 cc. of concentrated hydrochloric acid, or a corresponding amount of dilute acid. Boil until all the bromine is expelled, and add to the hot solution, with constant stirring, drop by drop, especially at first, 10 cc. of a 10 per cent. solution of barium chloride. Digest on the water-bath or over a low flame, with occasional stirring, until the precipitate settles clear quickly. Filter and wash, using either a Gooch crucible or a filter paper. The latter may be ignited moist in a platinum crucible, using a low flame until the carbon is burned.

"In the case of coals containing considerable pyrites or calcium sulphate, the residue of magnesium oxide should be dissolved in hydrochloric acid and the solution tested for sulphuric acid.

"If desirable, the burning of the coal with Eschka's mixture may be carried out in a muffle, from 20–30 minutes being required."]

Ultimate Analysis.

Determination of Carbon and Hydrogen :—These constituents are determined either by the methods given under Organic Analysis, or, if hydrogen is neglected, Ulgren's method of determining carbon may be used. See page 306.

Determination of Nitrogen :—See analysis of Guano.

Determination of Sulphur and Ash :—See Proximate Analysis.

[Determination of Oxygen* :—"The method to be used in calculating the oxygen of the coal presents , perhaps, the question of greatest difficulty. If we could be sure that all of the sulphur was present in the form of pyrites, and that this was converted into ferric oxide in the ash, the oxygen should be found by subtracting from 100, the sum of carbon, hydrogen, nitrogen, ash and five-eights of the sulphur. This is probably the best rule which can be given for general use, especially for coals high in sulphur. The chemist should, however, satisfy himself as to whether the ash is practically free from sulphates, and, if possible, whether the sulphur is mainly in the form of pyrites. If necessary, the rule should be modified, in particular cases, accordingly.

Determination of Heating Effect :—"In the preliminary report, the recommendation was made that the heating effect be given on the basis of the coal burned to vapor of water at 100° C. After some criticism from others and from further consideration, we have concluded to recommend that results be given for the coal burned to liquid water at the ordinary temperature. The reasons for this recommendation are that this appears to be the common practice in this country, and because coals are burned to liquid water in the bomb calorimeter, which undoubtedly furnishes the best determinations of heating effect at present available. Engineers and others will, of course, understand that the heating effect, when stated in this manner, includes from 3.5–4 per cent. of heat which can never be secured under the conditions of practical use.

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* [From Report of Committee on Coal Analysis, *ante*.]

"The most reliable formula for the calculation of the heating effect of a coal burned to liquid water, is that of Dulong, which gives the calorific power in calories per kilogram.

"Calorific power $= 8080\,C + 34{,}460\,(H - \frac{1}{8}O) + 2250\,S$.

"For the calculation of the oxygen, see above.

"The calorific power in British Thermal Units per pound may be found by multiplying that in calories per kilogram by nine-fifths.

"The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogram, by 536, or the number of B. T. U. per pound, by 965, and subtracting from this result, 1/7 more than the amount of water formed by burning 1 kilogram of the coal. The addition of 1/7 is given because the liquid water, on the basis of which the heating effect is given, must be considered as changed from water at ordinary temperature to steam at 100° C. The amount to be subtracted may be taken as 0.55 for most bituminous coals. The result gives the theoretical number of kilograms, or pounds, of water converted into steam from, and at, 100° C., by 1 kilogram, or pound of coal.

"The rule given, tentatively, in our preliminary report for the calculation of heating effect, from the amount of combustible matter present in bituminous coals, has been found to be of limited application."]

Determination of Heating Effect. Berthier's Method: —This method is based upon Welter's law, according to which the heat evolved by a fuel on combustion, is proportional to the amount of oxygen necessary to oxidize its carbon and hydrogen. Although, as Favre and Silbermann have shown, Welter's law is not strictly accurate,* for technical purposes it gives sufficiently accurate results.

Mix one gram of the finely pulverized and dried coal with 40 grams of litharge in a crucible, cover the charge with 30 grams of litharge and heat gradually to incipient redness, avoiding access of reducing gases. The temperature should be so regulated that the litharge is not completely melted until the coal is burned. After heating at a red heat for 45 minutes, the reduction will be complete. Either pour the charge, or allow to cool in the crucible, and then break, and clean the button of metallic lead.

34 parts of reduced lead correspond to 1 part of carbon. If a represents the amount of lead found, $a/34 . 100$ represents the relation of the heating value of the coal to that of pure carbon. If, for example, 1 gram of the fuel gave 10 grams of metallic lead, its heating value is $10/34 . 100=29.41$ per cent., as compared with pure carbon.

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* [For strictly accurate work, the heating value determined by Berthier's method must be corrected by a factor. This factor varies with different coals, and must be determined by comparison with a calorimeter.]

Forchhammer used a mixture of 3 parts litharge and 1 part lead chloride, instead of pure litharge, for the reduction. In some cases, (e. g. peat and wood), this mixture gives better results than litharge alone.

A considerable content of pyrites in the fuel makes the determination inaccurate, as it acts as a reducer on the litharge.

SODA ASH.

In the valuation of commercial soda, the determination of the content of Sodium Carbonate is generally sufficient; for this determination 2 different methods may be used. Either determine the carbon dioxide, or titrate a sample of the soda with a standard acid, and then compute the content of sodium carbonate.

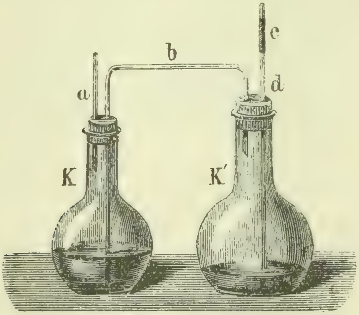

Fig. 55.

In the first method, the carbon dioxide is generally estimated by loss of weight, after treatment with an acid; less frequently, by direct weighing of the carbon dioxide.

Many forms of apparatus have been devised for estimating carbon dioxide by loss of weight, but only 2, Fresenius–Wills' and Mohr's, will be described in detail.

The former consists of 2 flasks, K and K′, Fig 55;

which are connected by a glass tube b bent twice at right angles. K contains the concentrated sulphuric acid for decomposing the sample, and K′ the solution of the carbonate. The glass tube d is closed on its upper end by a piece of rubber tubing and a piece of glass rod; the tube a is open at both ends. Fill K 1/2 full of concentrated sulphuric acid, and K′ 1/3 full of water. Place in K′ the sample, which has been previously dried at 100° C,* and weigh the entire apparatus.

Connect a piece of rubber tubing to a, and force a part of the sulphuric acid through b over into K′ to decompose the carbonate. Since the tube d is closed at c, the liberated carbon dioxide must escape through the remainder of the acid in K; this dries the gas. As soon as the evolution of gas in K′ ceases, force over more of the acid, and repeat this treatment until all the carbonate is decomposed. Now force almost all of the acid over into K′, and heat the contents of the flask, to expel the absorbed carbon dioxide. Remove the cap at c, and replace the carbon dioxide in the apparatus with air by suction on a. After the apparatus cools, weigh it again; the loss of weight represents the expelled carbon dioxide..

If the soda ash contains sulphides, sulphites or thiosulphates (commercial soda), hydrogen sulphide and sulphur dioxide will be expelled with the carbon dioxide. In such a case, boil the solution of soda with hydrogen peroxide, which will oxidize these compounds to sulphate. In the presence of chlorides, the liberated hydrochloric acid will render the result inaccurate; the latter may be avoided by adding a little silver sulphate.

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* The moisture may be determined by gently igniting a weighed sample.

The arrangement of Mohr's apparatus, which has an especial advantage when metals which form insoluble sulphates are present, is shown in Fig. 56. K is the

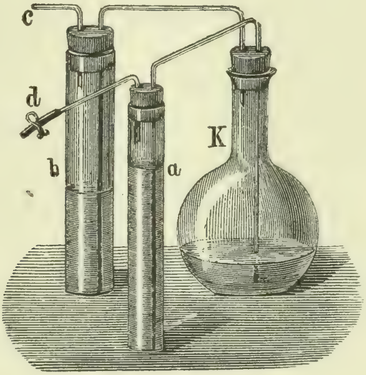

Fig. 56.

flask in which the substance is decomposed; it should have a capacity of about 100 cc.; a contains hydrochloric acid, and b concentrated sulphuric acid. Attach c to a suction pump, open the pinch-cock d, and suck a portion of the hydrochloric acid over into K, and at once close d, so that the carbon dioxide must pass through b, and thus be dried by the sulphuric acid.

When the evolution of gas has slackened, repeat the operation and finally allow the entire quantity of hydrochloric acid in a to pass over into K.

Now open the stop-cock d and remove the carbon dioxide in the apparatus by suction on c.

The other method of determining the amount of sodium carbonate in a sample of soda, consists in titrating the solution of the sample with an acid of known strength. For details, see Volumetric Analysis; Alkalimetry.

If the soda ash contains sodium hydroxide, sodium sulphide, or sodium thiosulphate, these compounds will be decomposed by the acid, and incorrectly calculated as carbonate. In such a case, proceed as given above, for the determination of carbon dioxide, after previously boiling the solution with hydrogen peroxide. To determine sodium hydroxide in the presence of carbonate, precipitate the aqueous solution of the soda with barium chloride, filter out the barium carbonate, and determine the sodium hydroxide volumetrically, in the whole, or an aliquot portion of the filtrate.

Sodium sulphide and sodium thiosulphate can both be determined by a standard solution of iodine. Acidify the solution of a fresh sample of the soda, with acetic acid, add starch solution and titrate with iodine. This gives the amount of sulphide and thiosulphate. Precipitate a second portion with ammoniacal zinc solution or manganous sulphate, filter out the zinc or manganese sulphide and determine the thiosulphuric acid in the filtrate, with iodine. The amount of iodine solution required for the sulphide is then found by difference. See Volumetric Analysis; Sodium Thiosulphate and Iodine Solution.

Instead of subtracting the amount of standard acid corresponding to the sodium sulphide found, and calculating the sodium carbonate from the difference, the sodium carbonate may be determined directly. For this determination, the above precipitate of barium carbonate is suitable, and the combined carbon dioxide may be determined either volumetrically or gravimetrically.

Fresenius determines both carbonate and sulphide in the same sample*, using the apparatus described on page 56. A weighed portion of the soda is decomposed with hydrochloric acid in the flask K. To condense the volatilized acid during the subsequent boiling, replace the bulb-tube b, by a vertical condenser. See page 58. The tubes f and g, are filled as before, To absorb the hydrogen sulphide, connect g with 2 U-tubes, filled with pumice stone saturated with copper sulphate (page 56), and calcium chloride. Connect these U-tubes with the soda-lime U-tubes, k and l.

Now proceed as given on page 56, with the difference that the liquid must be boiled for some time while passing a current of air, to expel the hydrogen sulphide. From the gain in weight of the copper sulphate and soda-lime U-tubes, the amount of hydrogen sulphide and carbon dioxide, respectively, may be calculated.

If the soda contains thiosulphate, the latter will be decomposed by hydrochloric acid with the formation of sulphur dioxide. The latter is absorbed by the soda-lime, and therefore calculated as carbon dioxide. The above method may be rendered applicable in this case, by interposing between the second copper sulphate U-tube, and the soda-lime U-tubes, a U-tube filled with chromic acid (see page 302) and a second U-tube filled with calcium chloride.

Commercial soda may also contain sodium chloride and sodium sulphate; these constituents may be determined in the usual manner. In the volumetric determination of sodium chloride by means of silver nitrate, first nearly neutralize the solution with nitric acid, leaving it very faintly alkaline. See Volumetric Analysis. Analysis by Precipitation.

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* Zeit. f. anal. Chem. Vol. 10, p. 75.

PEARL ASH.

In the analysis of this substance, the same determinations are made as given in the preceding example. If soda ash is admixed with the pearl ash, titration with an acid is of no value ; the content of potassium carbonate must then be separately determined. For this purpose, acidify the aqueous solution of the pearl ash with acetic acid, heat until all carbon dioxide is expelled, and precipitate the sulphuric acid with lead acetate. Cool the solution, dilute to a definite volume, and after the precipitate has settled, pipette out a definite volume and precipitate the excess of lead in it with hydrogen sulphide. Filter out the lead sulphide, add hydrochloric acid to the filtrate and evaporate to dryness in a weighed platinum dish. Weigh as $KCl+NaCl$. The potassium may now be separated as potassium-platinic chloride, or the chlorine may be determined either gravimetrically or volumetrically, and the potassium and sodium carbonates calculated from the chlorides.

SOAP.

In the valuation of soap, the constituents usually determined are Alkali, Fat, and Water. The alkali can easily be determined by titration with standard sulphuric or hydrochloric acid. Dissolve a weighed quantity of the soap in water, and titrate with standard acid, using blue litmus paper as an external indicator. If the titration has been made in a weighed porcelain dish, the same sample may serve for the determination of fat. Allow the acidified solution to cool, decant off the solution from the solidified fat, add distilled water and warm, to remove the rest of the alkali. After cooling, decant off the water and dry the fat at about 110° C., to constant weight.

If the soap contains sodium carbonate, it may be determined by expelling the carbon dioxide as given on page 56, or 381. A weighed quantity of the soap may also be extracted with absolute alcohol, the insoluble sodium carbonate filtered out, washed with absolute alcohol, dissolved in water and titrated with standard acid.

Determine the moisture by drying a weighed sample at 110–120° C., to constant weight.

NITER.

SALTPETER.

Principal constituent: Potassium Nitrate. Generally contains Sodium, Calcium and Magnesium Nitrates, Alkaline Chlorides and Sulphates.

If the niter contains no other nitrate, the potassium nitrate can be calculated from the nitric acid. As mentioned on page 323, nitrates, in the presence of hydrochloric acid and a ferrous salt, decompose to form ferric salt, water and nitric oxide. To determine the nitric acid, heat a weighed sample of the salt, without access of air, with a weighed excess of metallic iron or ferrous-ammonium sulphate (page 112) and hydrochloric acid. After complete decomposition, either titrate the excess of ferrous iron, with permanganate, or the ferric iron with stannous chloride. See Volumetric Analysis. The method of calculation is seen from the equation given on page 323.

In the valuation of a niter which contains nitrates other than potassium nitrate, the preceding method is not applicable. In such a case, the determination of the potassium is the only method to be relied upon. Transform the nitrates into chlorides by repeated evaporation with fuming hydrochloric acid. Determine the potassium as potassium-platinic chloride.

If the niter contains calcium or magnesium compounds, proceed as given on page 54.

Determine sulphuric and hydrochloric acids, as given on pages 24 and 26.

The moisture may be determined by drying a sample at 120° C.

GUNPOWDER.

Constituents: Niter, Charcoal, Sulphur, (Water).

The usual method for the analysis of gunpowder consists in drying a sample over concentrated sulphuric acid in a dessicator, or at 70° C. in an air-bath, and then extracting the niter by repeated washing with hot water on a weighed filter. Evaporate the filtrate to dryness in a weighed platinum dish, dry at 120° C. and weigh. The sum of carbon + sulphur is then obtained by difference. To determine the sulphur, extract the dried residue with carbon bisulphide or ammonium sulphide. The sulphur can now be calculated by difference, by drying the carbon to constant weight, or the carbon bisulphide may be evaporated and the sulphur then dried at 70° C., and weighed.

ANALYSIS OF ORGANIC COMPOUNDS.

I.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS.

The deportment of a substance when heated on a platinum foil, is generally used to decide whether or not it contains carbon. Most organic compounds are decomposed by this treatment, leaving a deposit of carbon. There are, however, a number of organic compounds, which volatilize without decomposition, or decompose without depositing carbon. If the above test, therefore, gives no positive result, mix a quantity of the substance with previously ignited copper oxide or lead chromate, and heat the mixture in a tube of difficultly fusible glass. This oxidizes the carbon to carbon dioxide, and the latter may be recognized by passing the gas into lime water.

Besides Carbon, organic compounds contain other elements. Hydrogen, Oxygen and Nitrogen are generally present; more rarely, Sulphur, Phosphorus, Chlorine, Iodine, etc.

Hydrogen is easily detected by the formation of water on heating a dry mixture of the substance and copper oxide or lead chromate. The water condenses on the cold walls of the tube; the water may also be driven over into a weighed calcium chloride U-tube, and its formation proved by the gain in weight of the U-tube.

Nitrogen is detected by first transforming it into a metallic cyanide, and then into Prussian blue. Heat a small portion of the substance with metallic sodium in a test tube, dissolve the mass in water, add ferrous sulphate and ferric chloride and then saturate with hydrochloric acid. A blue precipitate proves the presence of nitrogen.

Oxygen can neither be detected qualitatively nor determined quantitatively. Its presence in a compound is generally inferred, if, after determining the other constituents, the sum is not 100 per cent.

To detect sulphur, either oxidize the substance with nitric acid or aqua regia, or fuse it with a mixture of sodium carbonate and potassium nitrate or chlorate. The sulphuric acid found may be detected with barium chloride, as usual.

Phosphorus is detected in a manner similar to that for detecting sulphur. The phosphoric acid is easily recognized by its deportment with ammonium molybdate.

Only in rare cases, can chlorine be detected directly with silver nitrate, as many organic compounds containing halogous do not give a precipitate of silver chloride. The organic compound must first be decomposed, either by heating with nitric acid and silver nitrate, or by fusing with sodium carbonate and potassium nitrate.

Iodine is detecting in a similar manner. To detect metals in organic compounds, decompose the latter by ignition, extract the residue with an acid, and test as usual.

II.

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS.

ULTIMATE ANALYSIS.

Since in the oxidation or 'combustion' of carbon to carbon dioxide by heating with copper oxide, hydrogen is also oxidized to water, the 2 elements, carbon and hydrogen, are always determined at the same time. The products of the oxidation, carbon dioxide and water, are absorbed in suitable weighed apparatus, and from the gain

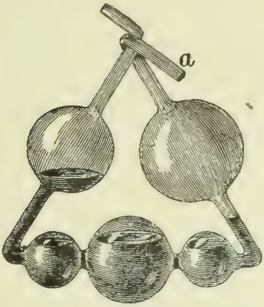

Fig. 57.

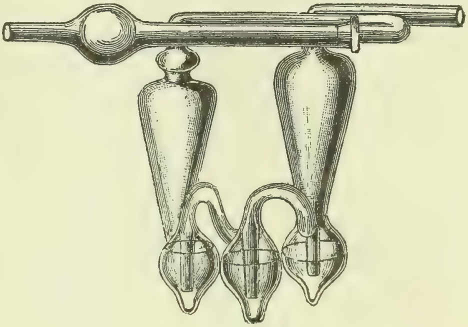

Fig. 58.

in weight after the combustion, the amount of carbon and hydrogen can easily be calculated.

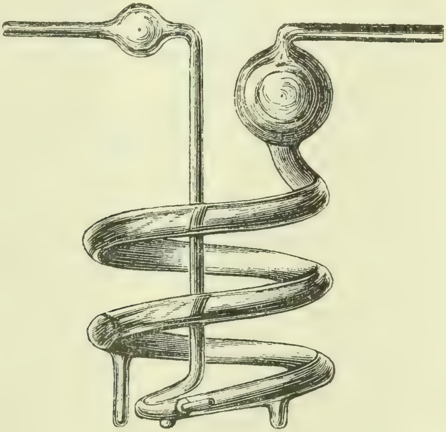

Fig. 59.

The carbon dioxide is absorbed in either a Liebig's bulb, Fig. 57, in Geissler's modification of Liebig's apparatus, Fig. 58, or in Winkler's apparatus, Fig. 59.

Liebig's or Geissler's apparatus is filled with pure potassium hydroxide, Sp. Gr. 1.2–1.3, by immersing the tube connected to the large bulb in the potassium hydroxide and applying suction to the other tube, until the 2 small bulbs are entirely full and the large bulb is half full, To avoid a possible loss of carbon dioxide, it is advisable to connect a U-tube filled with pieces of potassium hydroxide, with the main bulb. This precaution is especially advisable if the combustion is made with oxygen.

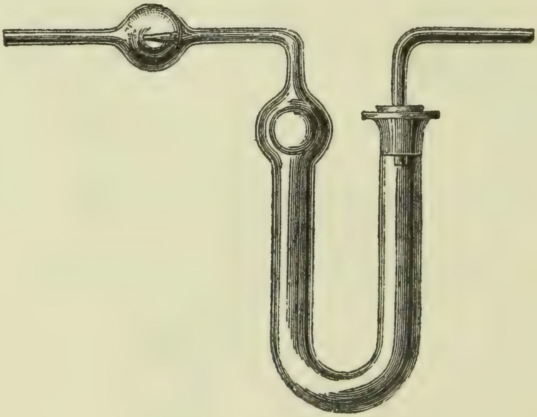

Fig. 60.

A tube filled with pieces of potassium hydroxide may also be connected directly with the bulb, as shown in Fig. 58.

A U-tube, Fig. 60, filled with granular calcium chloride, is generally used for retaining the water.

The bulb on the U-tube, serves to condense the greater part of the water, and should be placed in immediate connection with the combustion tube. Fill the bulb with cotton, then fill the 2 arms of the U-tube with calcium chloride, insert a loosely fitting wad of cotton, and stopper the arms with corks carrying pieces of glass tubing bent at a right angle.

Since calcium chloride frequently contains calcium hydroxide, it is necessary to pass dry carbon dioxide through the tube for several hours, and then to remove the carbon dioxide by passing dry air.

The apparatus shown in Fig. 61 is very suitable for absorbing the water; one of the arms contains a small stick of phosphoric acid, the other arm is partly filled with concentrated sulphuric acid.

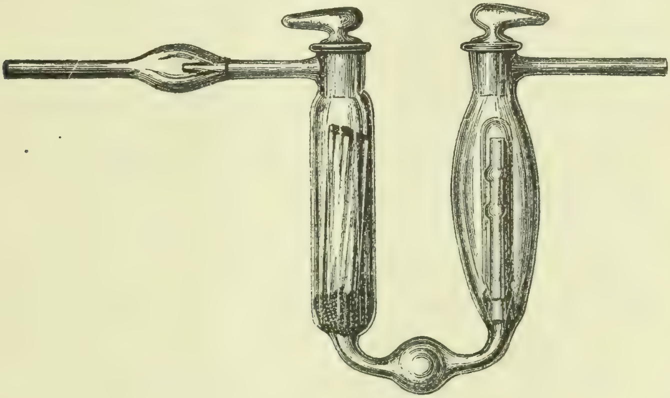

Fig. 61.

Select a combustion tube of difficultly fusible glass of about 2 mm. thickness, and of about 14 mm. inner diameter. The length of the tube will depend upon the length of the furnace used. Take a tube long enough to make 2 combustion tubes, heat in the middle with the blast lamp, draw it out and bend it to the form shown in Fig. 62.

The tube must be carefully cleaned and dried before being used. The best way to remove moisture is to heat the tube on a sand-bath or in a combustion furnace, and to blow dry air through a glass tube that reaches to the extreme end of the combustion tube.

The hot tube should be closed with a stopper carrying a calcium chloride tube, to prevent access of moisture.

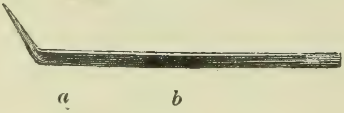

Fig. 62.

Organic substances are oxidized with copper oxide, lead chromate, or oxygen. In the case of difficultly combustible substances, and those that contain sulphur, the alkalies or alkaline earths, lead chromate must be used.

Combustion with Copper Oxide or Lead Chromate :*—The granular copper oxide must be freed from water and organic matter, previous to use, by ignition in a copper crucible. Place the copper oxide while still warm, in a dry flask, Fig. 63, and stopper with a cork provided with a calcium chloride tube; these precautions are necessary to protect the oxide from dust and moisture. Preserve lead chromate in a similar manner.

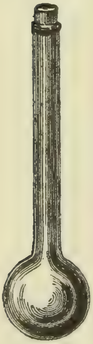

Fig. 63.

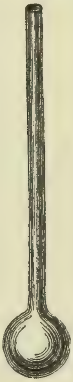

Fig. 64.

The substance is weighed out exactly as given on page 7. If the substance is liquid, weigh it in the bulb shown in Fig. 64.

The bulbs may be filled by gently warming over a flame, immersing the tip in the liquid, and after a little of the latter has sucked in, again heating to expel the air and fill the bulb with the vapor of the substance. On again immersing the tip in the substance, the tube will be entirely filled, when the vapor condenses. Fuse the tip together, and determine the gain in weight.

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* Substances containing sulphur should be burned with lead chromate instead of copper oxide. Asbestos impregnated with lead chromate, has been recommended.

To make a combustion, fill the combustion tube, Fig. 62, up to a with granular copper oxide, place the substance in the tube, add copper oxide up to b and mix it with the substance by means of the copper wire shown in Fig. 65. Now fill the tube from b to c with copper oxide and insert a loose plug of ignited asbestos. Tap the tube on the table to form a canal for the passage of the gases formed, place the tube in the combustion furnace and connect with the absorption apparatus.

Fig. 65.

In the combustion of liquids, scratch the tip of the tube (Fig. 64) with a file, break off the tip and slide the tube and tip down into the partly filled combustion tube. In the case of very volatile substances, it is advisable to break the bulb after placing in the combustion tube. This may be done by shaking the tube, or by gentle heating. Now heat the forward part of the tube, c, to incipient redness, and gradually heat backward toward a, so that a large layer of the copper oxide is at a red heat before the substance begins to decompose. Care must be taken that the decomposition does not proceed too rapidly, as the combustion may be imperfect and a portion of the substance be volatilized before decomposition. The condensation of water on the cool end of the tube must also be guarded against; if any water has so condensed, it may be driven over into the U-tube by gently warming with a small flame.

When the entire length of the tube in the furnace is at a red heat and no more bubbles are passing over into the absorption apparatus, break off the tip d, and sweep over all the carbon dioxide by passing pure oxygen through the train. Finally remove the absorption apparatus, close the ends with rubber tubing caps, cool and weigh.

In the analysis of compounds which contain chlorine, bromine or iodine in addition to carbon, hydrogen and oxygen, a longer combustion tube must be used. Place a roll of copper or silver foil in the end of the tube next to the absorption train; the foil should be heated to a red heat before being placed in the tube. Likewise in the analysis of nitrogenous substances, a spiral of reduced copper gauze should be placed in the same end of the tube.

Combustion in a Current of Oxygen:—Very difficultly combustible substances, and those which leave a residue after combustion are generally burned in a platinum boat in a current of oxygen; in this case, it is preferable to absorb the carbon dioxide in 2 U-tubes filled with soda-lime. In order to avoid any loss of moisture which might be volatilized by the heat generated when the carbon dioxide is absorbed by the soda-lime, the U-tubes should be filled but 2/3 full with soda-lime and the remainder with phosphorus pentoxide. Separate the 2 substances by wads of glass wool. Use a combustion tube open at both ends, Fig, 66;

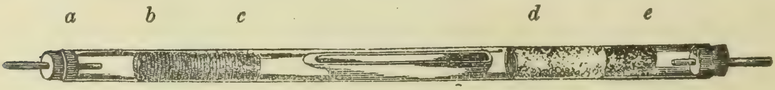

Fig. 66.

place the roll of copper gauze at b c, fill the part d e with granular copper oxide, and stopper loosely with asbestos. First heat the tube while passing a current of oxygen, to oxidize the copper and remove all moisture; stopper the

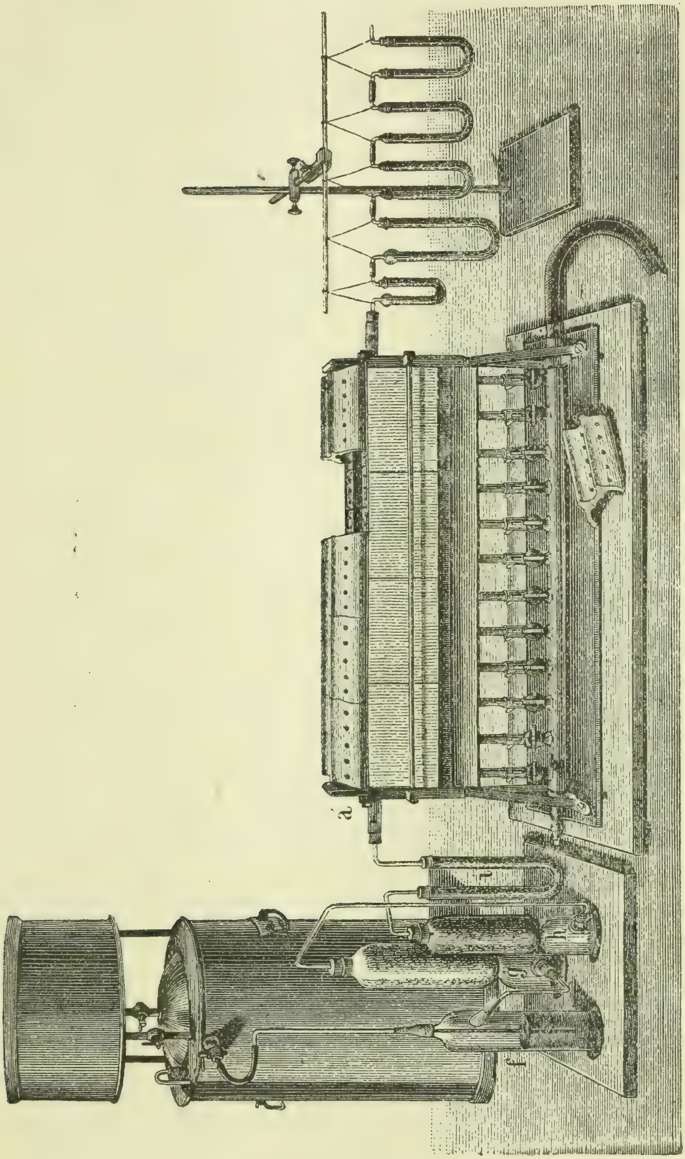

Fig. 67.

tube with corks, one of which is provided with a calcium chloride tube, and allow the tube to cool.

Remove the stopper at a, and the roll b c, place the boat containing the substance between c and d, replace the copper gauge and connect a with the oxygen gasometer. The arrangement of the apparatus is shown in Fig. 67. To make a combustion, first heat the part of the tube d e containing the copper oxide, then the part b c, up to red heat, then gradually increase the temperature between c and d by lighting the burners under that portion of the tube, at the same time passing a current of oxygen.

The oxygen must be perfectly dry and free from carbon dioxide. Before entering the combustion tube, it should, therefore, be passed through the train f, g, h and i, Fig. 67, filled with concentrated potassium hydroxide, pumice stone saturated with concentrated sulphuric acid, potassium hydroxide in sticks and calcium chloride, respectively.

Determination of Nitrogen:—The method is based upon the fact that nitrogenous organic substances, when ignited with an alkaline hydroxide, form alkaline carbonate, while the hydrogen of the hydroxide unites with the nitrogen to form ammonia.

Use a mixture of 1 part sodium hydroxide and 2 parts soda-lime. The ammonia is absorbed in dilute hydrochloric acid and subsequently precipitated as ammonium-platinic chloride, and weighed. The ammonia may also be absorbed in an excess of standard acid, and the excess titrated back with standard alkali.

If, for example, 10 cc. of oxalic acid solution containing 0.6285 gram $H_2C_2O_4 . 2H_2O$, or 10 cc. of sulphuric acid containing 0.4891 gram of H_2SO_4, were used, this amount would correspond to 0.1401 gram of nitrogen.

Varrentrap-Will's apparatus, Fig. 68, or Arendt-Knop's apparatus, Fig. 69, may be used to absorb the ammonia.

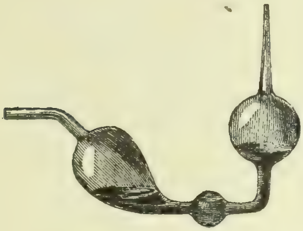

Fig. 68.

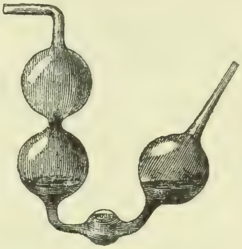

Fig. 69.

The latter has the advantage that the second bulb is a safeguard against the solution sucking back into the combustion tube.

If the ammonia is to be determined volumetrically, Peligot's absorption apparatus, Fig. 70, is especially to be recommended.

For the ignition, use a tube of difficultly fusible glass about 40 cc. long, drawn out at one end to an upward inclined tapering tip, Fig 62. Fill the rear end of the tube with soda-lime* for about 10 cm., add the substance, then another layer of soda-lime about 10 cm. in length, and mix with the wire shown in Fig 65. Fill the front end of the tube with a layer of soda-lime about 15 cm. long. The front end of the tube should have a vacant space of about 5 cm. Close the tube with a loose plug of ignited asbestos, and form a canal for the passage of the gas by tapping on the table.

Connect the tube with the absorption apparatus.

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* The soda-lime should contain no nitrous acid, and it should previously be ignited.

First heat the front layer of soda-lime, and then gradually increase the temperature toward the rear end of the tube.

In the case of substances having a high content of nitrogen, the absorption of the ammonia may be so sudden as to cause the solution to suck back into the combustion tube, and spoil the combustion. Such substances should be mixed with an equal amount of pulverized sugar; the ammonia is then diluted with the products of decomposition of the sugar and the rate of absorption moderated. The forward end of the combustion tube should not be heated too strongly as there is danger of dissociating the ammonia.

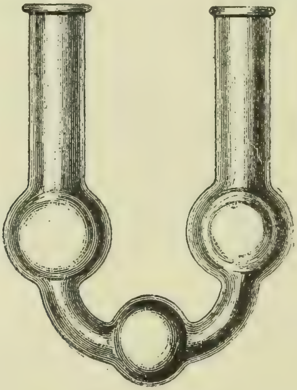

Fig. 70.

When the combustion is finished, break the tip of the combustion tube and aspirate air through the tube for a short time.

To determine the ammonia gravimetrically, rinse the contents of the absorption apparatus into a porcelain dish and proceed as given on page 109.

194.43 parts of platinum correspond to 28.02 parts of nitrogen.

In determining nitrogen in fertilizers which contain potassium nitrate, the method suggested by John Ruffle* is to be recommended. Ruffle used a mixture of sodium thiosulphate and soda-lime, instead of the latter alone, and an iron tube, instead of a glass tube. Grind together 6 parts by weight of soda-lime and 7 parts by weight of crystallized sodium thiosulphate, also mix 1–1.5 grams of the substance with 1 gram of a mixture of equal parts of flowers of sulphur and pulverized charcoal. Fill the iron tube as follows: Place about 5 grams of the soda-lime and thiosulphate in one end of the tube, then about 30 grams of the same mixture intimately mixed with the substance, then a layer of soda-lime and thiosulphate and finally a layer of pure soda-lime. First heat the soda-lime to redness, and then heat the remainder of the tube. After igniting at a red heat for 10 minutes, the decomposition is complete. The ammonia is absorbed and treated as given above.

Absolute determination of Nitrogen:—This method, originally devised by Dumas, is executed as follows: Use a combustion tube fused together at one end. Fill in about 10 cm. of coarsely granular magnesite, then an equal amount of copper oxide, then the substance mixed with copper oxide and finally a roll of copper gauze about 20 cm. long. The nitrogen formed during the combustion is collected on a pear-shaped vessel, Fig. 71; the latter is provided with an exit tube which can be closed with a pinch-cock during the combustion. The vessel is filled with mercury and potassium hydroxide solution.

Before connecting the vessel with the combustion tube, heat the rear layer of magnesite to expel the air.

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* Jour. Chem. Soc., 1881. p. 87.

When all the air has been expelled (as shown by collecting a small sample in a test tube over potassium hydroxide), connect the apparatus, allow the magnesite to cool and begin the combustion by heating the copper spiral to redness and then heating the portion of the tube containing the substance.

When all the nitrogen has been driven over by again heating the magnesite, transfer the gas to a eudiometer for measurement. For this purpose, place in the tubulure of the holder, a tube of the form shown in Fig. 72, and pour in sufficient mercury to drive the potassium hydroxide solution above the rubber tubing.

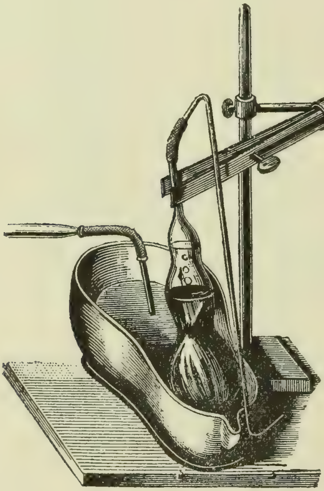

Fig. 71.

Before the measured volume obtained can be calculated to the corresponding weight, the gas volume must be reduced to standard conditions of temperature and pressure.

If V′ represents the unknown volume of nitrogen at 0°C and 760 mm. pressure,

V the observed volume,

H the observed barometric height,

h the height of the mercury in the eudiometer,

t the temperature of the nitrogen,

f the tension of water vapor at t°C, and

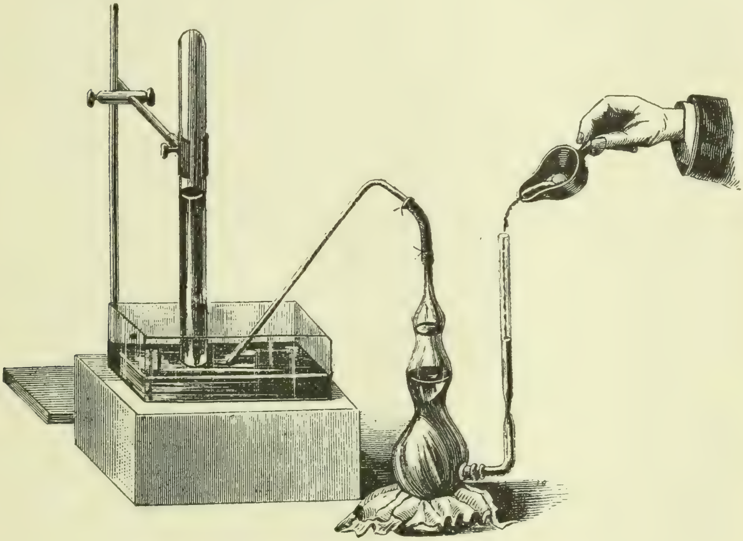

Fig. 72.

α the coefficient of expansion of the gas (0.003665), then,

$$V' = \frac{V(H-h-f)}{(1+\alpha t)760}$$

From this volume, the weight of the nitrogen may be obtained by multiplying by the weight of 1 cc. of nitrogen, 0.001256.

Instead of generating carbon dioxide by heating magnesite, it is preferable to generate it in a special generator and to connect the latter with one end of the combustion tube. In this case, interpose between the tube and the generator, the necessary wash bottles, and a calcium chloride tube provided with a stop-cock.

[The nitrogen may be collected in a Schiff's azotometer, in which it may be measured direct. The troublesome transferring of the nitrogen to a measuring tube, is thus avoided. The combustion tube should be sufficiently long to project about an inch and a half at each end of the furnace to prevent scorching the stoppers. Fill the tube as follows, commencing at the exit end of the tube: First insert a spiral of copper gauze about 2 cm. long, about 12 cm. from the end, add enough coarse copper oxide to make a layer about 30 cm. long, and then insert another short plug of copper gauze. The substance to be analyzed, is now added. If it is a powder, it is mixed with enough fine copper oxide to make a layer about 10 cm. long, and a short plug of copper gauze is then added; if it is a liquid, it is filled into a glass bulb, Fig. 64, then placed in a boat made of copper foil, and shoved into the tube. Back of the substance, there is placed a spiral of oxidized copper gauze, about 10 cm. long. In the exit end of the tube, place a spiral of reduced copper gauze, about 10 cm. long, to reduce any oxides of nitrogen that might be formed during the combustion. The oxides of nitrogen, being acid in nature, would be absorbed by the potassium hydroxide, and lost in the analysis. The spiral may be reduced as follows: Place about 1 cc. of methyl alcohol in the bottom of a test-tube large enough to receive the spiral; the spiral, held by crucible tongs, is then heated to glowing in a large, somewhat roaring blast-flame, and then dropped as quickly as possible into the test-tube. The dark spiral is reduced to bright metallic copper, while vapors having a sharp, pungent odor, which frequently ignite, are formed. After a few minutes, stopper the test-tube, and allow the spiral to cool.

Connect the combustion tube with the azotometer (containing 1 : 1KOH) on one end, and with the carbon dioxide generator, on the other end, and pass a rather rapid current of carbon dioxide through the train, to sweep out all the air. During this operation, the upper stop-cock of the azotometer should be open, and the pear as low as possible, so that it contains the most of the potassium hydroxide solution. After a rapid current of carbon dioxide has been passing for about 15 minutes, the burners under the copper spiral should be lighted in order to expel any occluded gas (hydrogen). Now raise the pear high enough to cause the potassium hydroxide solution to ascend somewhat above the stop-cock, close the latter, and then lower the pear as far as possible. When the air in the train has been completely replaced by carbon dioxide, only a minimum amount of light foam should collect over the potassium hydroxide in the course of 2 minutes. Otherwise, open the stop-cock, refill with potassium hydroxide, and test again.

Now heat the layer of coarse copper oxide to incipient redness, heat the spiral of copper back of the substance, while passing a slow current of carbon dioxide. The combustion must be so regulated that the bubbles of gas ascend with a slow regularity. When the gas no longer collects, as shown by the complete absorption of the gas bubbles by the potassium hydroxide solution, gradually turn out the burners, pass a rapid current of carbon dioxide for about 10 minutes, close the pinch-cock at the foot of the azotometer, and allow the latter to assume the temperature of the room.

The calculation of the analysis is rendered very simple by referring to the table in the back of the book, in which the weight of 1 cc of moist nitrogen is given in milligrams, for different temperatures and pressures. This modification has the disadvantage that the tension of concentrated potassium hydroxide is not exactly known, and therefore a somewhat arbitrary correction must be applied, for strictly accurate work. For ordinary work, however, the correction may be neglected.]

VOLUMETRIC ANALYSIS.

The distinction between Volumetric Analysis and Gravimetric Analysis has been indicated in the Introduction. The determination of silver by means of a standard solution of sodium chloride, devised by Gay-Lussac, was the first volumetric method. Since this method of analysis requires the accurate measurement of solutions, it is called Volumetric Analysis. To facilitate calculations, normal solutions are generally used; empirical solutions are used only when the strength decreases rapidly. A normal solution contains the hydrogen equivalent* of the active reagent, expressed in grams, in a liter.† Thus, normal oxalic acid contains $\frac{125.7}{2} = 62.85$ grams of crystallized acid in a liter: normal hydrochloric acid, 36.37 grams; normal sulphuric acid, $\frac{97.82}{2} = 48.91$ grams; normal nitricacid, 62.89 drams; normal potassium hydroxide, 55.99 grams; normal sodium thiosulphate, 247.62 grams; normal iodine, 126.54 grams, in a liter.

If a liter of the solution contains 1/10 of the equivalent, it is designated tenth normal, if 1/100 of the equivalent, hundredth normal, etc.

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* A hydrogen equivalent is that amount which brings 1 gram of hydrogen into chemical reaction, either directly or indirectly.

† [Since the ratio between hydrogen and oxygen is not 1:16, but 1:15.88, and since 0=16, is at present adopted as the standard, it would seem more logical to make a normal solution of such concentration as to contain an amount of the substance equivalent to 8 grams of oxygen.]

As above mentioned, in volumetric analysis the quantity of the substance sought is determined by measuring the volume of the solution required to transform the substance into another chemical compound. The point at which the action is complete must be shown by certain phenomena, generally color changes. In the determination of alkalies by a standard acid, the end of the reaction is shown by the indicator, litmus tincture, changing in color from red to violet. In other methods, other color changes appear. The accuracy of a volumetric method depends in part, therefore, upon the observation of color changes; the more suddenly the indicator changes color, the more accurate must be the results. Volumetric methods may be divided into the following groups.

I.

ANALYSIS BY SATURATION.

To this class belong:

1. Alkalimetry. Determination of alkalies by a standard acid;

2. Acidimetry. Determination of acids by a standard alkali.

Both methods depend upon neutralization.

Indicators.

Litmus tincture was formerly exclusively used as an indicator in neutralization. The use of litmus, however, has the disadvantage that in the determination of the alkaline carbonates, the carbon dioxide liberated on adding the acid changes the color from blue to violet, so that it is necessary to expel the carbon dioxide by boiling. A number of other indicators have been recommended and brought into use, to replace litmus tincture; these indicators possess advantages in varying degree. However, as litmus is still much in use, the following notes on its preparation may be of value. In preparing the tincture, use the commercial cube litmus. Extract the litmus with water, filter out the insoluble matter, add ammonium chloride to the filtrate and boil as long as moistened red litmus paper is turned blue. There is thus obtained a bluish violet liquid which is changed to blue by the slightest amount of alkali, and red by the slightest amount of acid. The tincture cannot be preserved in closed vessels, as mould forms in the solution; it is best to close the flask loosely with a plug of cotton. Among the other substances which have been recommended as indicators in saturation analyses, the following may be mentioned:

Phenolphthalein:—This substance is used in alcoholic solution (1:25). If a drop of the colorless solution is added to a solution of a fixed* alkali, the solution is colored intensely red; the solution is again decolorized by the slightest amount of free (also carbonic) acid.

Methyl Orange:—This indicator is effected but slightly by free carbonic acid, so that it may be used in the direct titration of alkaline carbonates, without boiling the solution. The aqueous yellow solution is not changed by alkalies; with free acids, the color changes to red. Use a solution containing 1 gram of methyl orange in a liter; about 4 drops should be used for each 100 cc. of solution. Methyl orange cannot be used in the titration of alkalies with oxalic acid.

Corallin:—The aqueous solution, containing with hydrochloric acid, is colored red by alkalies.

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* Phenolphthalein cannot be used to titrate ammoniacal solutions.

Fluorescein :—This substance is of especial value in the titration of cloudy or colored solutions. Use a very dilute alcoholic solution, and add sufficient indicator to the solution being titrated to render visible the green fluorescence. Free acids destroy the fluorescence and produce a yellow color.

Phenacetolin :—Dissolves in alkaline hydroxides and forms a pale yellow colored solution. If dissolved in alkaline carbonates, an intensely red color is produced.

An alcoholic solution is, therefore, suitable as an indicator in the determination of alkaline hydroxide and carbonates in admixture. If sufficient phenacetolin is added to a solution of the two substances to color it a pale yellow, and the solution is then titrated with sulphuric acid, the color changes through rose color to a deep red as soon as the alkaline hydroxide is neutralized ; a further addition of acid changes the color to a golden yellow. The number of cubic centimeters of acid required to give the first color change, corresponds to the amount of alkaline hydroxide present, and the remainder to the alkaline carbonate present.

II.

ANALYSIS BY OXIDATION AND REDUCTION.

All substances which can be reduced to a definite lower state of oxidation by a reducing agent and then be reoxidized to the higher state by an oxidizing agent, belong to this class. The oxidizing agent is used in the form of a standard solution, and the amount of the latter used corresponds to the amount of the substance oxidized. The most important oxidizing agents are Potassium Permanganate and Iodine. If permanganate is used, the end of the reaction is shown by the red color of the solution, produced by a slight excess of the reagent. With iodine, starch solution is used as an indicator; the slightest excess of iodine produces the blue iodide of starch*.

To this class of analysis belongs, for example, the determination of iron. The iron, present in solution in the ferrous condition, is oxidized by a standard solution of potassium permanganate. From the amount of permanganate used, the content of iron may easily be calculated.

III.

ANALYSIS BY PRECIPITATION.

Those analyses in which the end of the reaction is shown by the beginning or end of the formation of a precipitate by the addition of the reagent, belong to this class of analysis. Examples of this class are: the determination of silver with a standard solution of sodium chloride and the determination of phosphoric acid with a standard solution of uranium acetate.

Apparatus Used in Volumetric Analysis.

As mentioned above, volumetric analysis depends upon the measurement of volumes of liquids, while gravimetric analysis depends upon the determination of the weight of solids. The manner of substituting the former for the latter, is very simple. If, for example, 1 gram of a salt is dissolved in 10 parts by volume of water, and 1 part of this solution is measured from a burette, this 1 part will contain 1/10 gram of the salt. If 1 gram of a salt is dissolved in 1000 volumes of water, 1 volume of this solution will contain 1/1000 gram of the salt. If the solution is made more dilute, e. g. by dissolving 1 gram of the salt in 10,000 or 100,000 volumes, portions of the salt far too small to be weighed, can be determined.

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* As starch solution soon spoils, a small amount should be prepared shortly before use. Make a paste of a piece of starch the size of a bean in 1–2 cc. of cold water, and pour into about 300 cc. of boiling water. If the solution is boiled for a few minutes, it becomes transparent and need not be filtered.

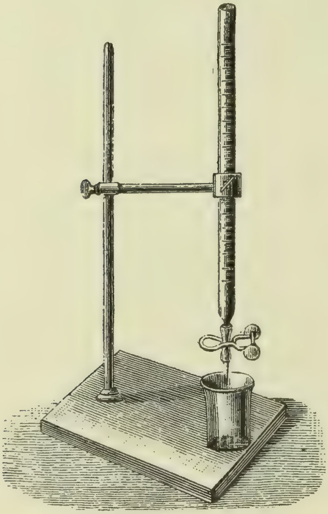

Fig. 73.

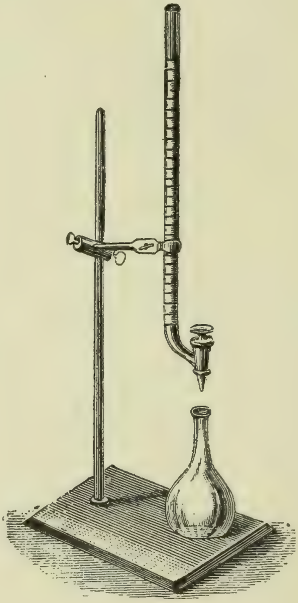

Fig. 74.

The replacement of weighing by measurement of volumes presupposes a system of weights and measures in which the unit mass and unit volume have a simple relationship; this is the case in the Metric System.

To prepare a liter flask such as is used in making up standard solutions, weigh 1 kilogram of boiled, distilled water at 4.°C. in a narrow necked flask and mark the bottom of the meniscus on the glass with a diamond. If the flask and water are now taken to a room in which the temperature is about 16.°C., the water gradually warms and expands, so that the level of the liquid rises above the mark.

It is self-evident, that if the liter flask is filled with water at 16.°C., the weight of the quantity of water is not 1 kilogram, but considerably less. The expansion of water must, therefore, be considered in marking the flask. If the volume of 1 gram of water at 4.°C is placed = 1, then the volume at

12°C. = 1.000456
13 “ = 1.000570
14 “ = 1.000703
15 “ = 1.000847
16 “ = 1.000997
17 “ = 1.001162
18 “ = 1.001339
19 “ = 1.001527
20 “ = 1.001731

1000 cc. of water at 4°C. expand to 1001.16 cc. when warmed to 17°C., and to 1001.73 cc., when warmed to 20°C.

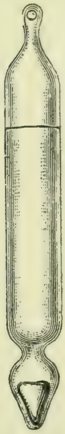

Fig. 76.

In preparing a liter flask, therefore, it is preferable to use water at 16°C., rather than water at 4°C. as the error due to differences in temperature in different rooms will be smaller. The flask must have a rather narrow neck so as to avoid magnifying the error of reading; furthermore, there must be sufficient room between the stopper and the mark, to allow mixing. The exact position of the meniscus may be determined by holding it on a level with the eye.

Besides the liter flask, flasks of 500, 250, 200, 100 and

50 grams, are used. The use of graduated mixing cylinders is less desirable, since the error of reading is too great.

The solutions used in analysis are generally measured in burettes. The pinch-cock burette, first constructed by Mohr, is shown in Fig. 73. On account of the rubber connection, however, Mohr's burette cannot be used for potassium permanganate or iodine. Geissler modified Mohr's burette, as shown in Fig. 74. This form is undoubtedly preferable to all other forms.

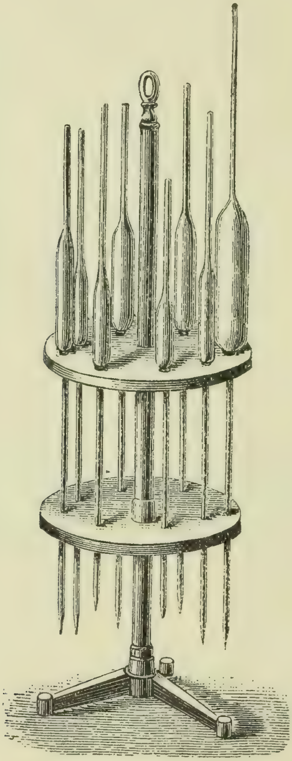

Fig. 76.

In a narrow tube, the surface of a liquid assumes a concave form, the appearance of which depends upon whether it is seen against a light or a dark background.

Various means may be used for determining the lowest point of the meniscus. The sharpest reading can be obtained by clamping a strip of black paper upon a larger sheet of white paper, and then holding the black strip just below the bottom of the meniscus.

To facilitate reading burettes, Erdmann has contrived the float shown in Fig. 75; the lower part of the float is filled with mercury.

There is a fine mark around the float, to indicate the position of the liquid. In using the float, the surface of the liquid is not observed, but only the position of the mark on the float. Since the position of the mark, with respect to the surface of the liquid, always remains the same, correct readings are obtained. Before making a titration, lower the mark to zero.

Instruments which serve to remove a definite portion of the liquid from another vessel, by the aid of suction, are called pipettes. Pipettes generally have 2 marks, between which their volume is contained. 100, 50, 25, 20, 10 and 5 cc., are the sizes most used. Fig. 76 shows a pipette stand with an assortment of pipettes.

ALKALIMETRY.

DETERMINATION OF ALKALIES.

The determination of alkaline hydroxides and carbonates by means of a standard acid, is called Alkalimetry. Alkalimetry may also be extended to include the determination of the alkaline earth hydroxides and carbonates, and also magnesia. The principle of alkalimetry has been pointed out in the Introduction; a standard acid is added to the solution of a weighed sample of the substance, until neutralization ensues. The neutralization point is shown by an indicator (see above).

Either oxalic, hydrochloric, sulphuric or nitric acid may be used in the preparation of the normal acid. As oxalic and sulphuric acids form difficultly soluble compounds with barium, strontium and calcium, they are not as suitable as hydrochloric or nitric acid.

Normal Oxalic Acid:—Crystallized oxalic acid has the formula, $H_2C_2O_4+2H_2O$; its equivalent weight is, therefore, $\frac{125.7}{2}=62.85$. Weigh out 62.85 grams of pure, crystallized oxalic acid, transfer to a liter flask and dissolve in about 500 cc. of water. When the acid is in solution, fill the flask nearly to the mark, adjust the temperature to that at which the flask was calibrated and then add water until the bottom of the meniscus coincides with the mark.

Normal hydrochloric acid must contain 36.37 grams of HCl in a liter. Use the pure acid and dilute it with the necessary amount of water. To determine the content of HCl in the ordinary acid, determine the Sp. Gr. or degrees Beaume of the aqueous acid. If, for example, the acid has a Sp. Gr. of 1.108, (corresponding to 14° Beaume), the content of HCl is 21.5 per cent. Therefore, to prepare 1 liter of normal hydrochloric acid, 152.6* cc. of acid must be dilated with 847.4 cc. of water.

To prepare normal nitric acid, 62.89 grams per liter, or normal sulphuric acid, $\frac{97.82}{2} = 48.81$ grams per liter, proceed in a similar manner. In every case, it is necessary to determine the concentration of the acid by a special experiment. Pure sodium carbonate is generally used for this purpose, and may be obtained by gently heating the bicarbonate. Dissolve a weighed sample of the pure sodium carbonate in water, and ascertain how much of the acid is necessary to neutralize it. If, for example, hydrochloric acid is being titrated, 1000 cc. of it, which contain 36.37 grams of HCl, must correspond to 52.925 grams of sodium carbonate. Suppose 1.056 grams of sodium carbonate were taken ; if the acid is normal, $52.925 : 1000 = 1.056 : x, = 19.95$ cc. would be required. If 19 cc., instead of 19.95 cc., were used in the titration, and the amount of solution still in the flask is 940 cc., the latter must be diluted with water to $(19 : 19.95 = 940 : x, =)$ 987cc.

In the execution and calculations of alkalimetric determinations, it should be remembered that,

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[*] $\frac{100}{1.108} : 21.5 = x : 36.37. \qquad x = 152.6.$

1 Equivalent of Potassium Oxide = 47.01 grams,
1 " " Potassium Carbonate = 68.955 grams,
1 " " Sodium Carbonate = 52.925 grams,
1 " " Ammonia = 17.01 grams.

If 4.701 grams of potassium oxide are weighed out, 100 cc. of normal acid will be required to neutralize it. If the potassium oxide used was not pure, the number of cubic centimeters of acid used expresses the content of K_2O. K_2O is capable of existence only in combination with water, as KOH; if an amount of KOH equivalent to K_2O (4.701) is weighed out, each cubic centimeter of acid used corresponds to 1 per cent. of K_2O.

If the equivalent of potassium hydroxide is weighed out, the number of cubic centimeters of normal acid used, expresses the percentage of KOH in the sample.

1 equivalent of sodium carbonate, 52.925 grams, requires, e. g., 1 equivalent of oxalic acid, 62.85 grams; 5.298 grams of sodium carbonate would require 100 cc. of normal oxalic acid, and each cubic centimeter would represent 1 per cent. of pure sodium carbonate. From this it is seen that by weighing out an equivalent weight of the substance to be analyzed, the calculation is very much simplified.

With hygroscopic substance, e. g., potassium carbonate, and those which absorb carbon dioxide from the air, e. g., posassium hydroxide, and sodium hydroxide, and also in the analysis of solutions, it is neither practicable nor advisable to weigh out definite amounts. In such cases, weigh out an arbitrary amount of the substance, and titrate.

If S represents the number of cubic centimeters of normal acid used, e. g., in the determination of the amount of KOH in commercial caustic potash,

$$1000 : 55.99 = S : x.$$

$$x = \frac{55.99\ S}{1000} \text{ grams KOH.}$$

If A represents the weight of the sample used, then

$$A : \frac{55.99\ S}{1000} = 100 : x,$$

and

$$x = \frac{5.599\ S}{A} \text{ per cent. KOH.}$$

The determination of caustic alkalies by means of an acid of known strength, is a very simple operation ; it is simply necessary to add an indicator, e. g., litmus tincture, and then add acid until the blue color changes to violet red. In titrating alkaline carbonates, the liberated carbon dioxide produces a color change in the indicator similar to the end reaction, unless methyl orange is used as indicator. In the determination of alkaline carbonates, it is, preferable, therefore, to add an excess of normal acid, boil to expel the carbon dioxide, and then titrate back with normal alkali. Mohr used sodium hydroxide* for this purpose. Since, however, it is not possible to prepare sodium or potassium hydroxide entirely free from carbon ate,† there is not much gained in so doing.

If the normal potassium hydroxide is to be equivalent to the normal acid, it must contain 55.99 grams of KOH per liter. 1 cc. of the solution then corresponds to 1 cc. of normal acid. An approximately normal solution is pre-

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[*] Potassium hydroxide is preferable to sodium hydroxide, since the latter strongly attacks glass.

[†] [Compare preparation of sodium hydroxide free from carbonate, (Garrigues' Method) p. 300.]

pared by dissolving 55.99 grams of purified KOH in 1 liter of water, and titrating against the normal acid, as given above.

Standard ammonium hydroxide is far preferable to sodium or potassium hydroxide, as it may easily be prepared free from carbonate, and does not attract carbon dioxide from the air. As concentrated ammonium hydroxide continually gives off ammonia, normal solutions can not be prepared. It is preferable, therefore, to prepare a very dilute ammonium hydroxide solution, and then determine its relation to the normal acid by a special experiment. An ammonium hydroxide solution of Sp. Gr. .9932 (1.6 per cent. NH_3). changes but slightly in well-closed bottles. Of course, the titration must be made in a cold solution.

In the determination of caustic alkalies in the presence of alkaline carbonates, first determine the amount of normal acid necessary to saturate the total alkali present, in one sample, and then boil the solution of a second sample with barium chloride. Dilute the solution to a definite volume, allow the precipitate of barium crrbonate to settle, pipette out a sample and determine the caustic alkali with normal acid (see below). The precipitate of barium carbonate may also be filtered out and titrated with normal nitric or hydrochloric acid (see below).

By using phenacetolin as indicator, caustic alkali and alkaline carbonate, may be determined in the same solution.

To determine bicarbonates, add barium or calcium chloride to the solution, and titrate the precipitated barium or calcium carbonate, as given above.

Determination of Carbon Dioxide in Soluble Carbonates :—The determination of the alkalies is also a determination of carbon dioxide. If t cubic centimeters of normal oxalic acid were used in neutralizing a quantity A of a carbonate, since 1000 cc. = 62.85 grams of oxalic acid, and this amount corresponds to 21.945 grams of carbon dioxide, the following is obtained :

$$1000 : 21.945 = t : y ;$$

$$y = \frac{21.945\ t}{1000}$$

$$A : \frac{21.945\ t}{1000} = 100 : x ;$$

$$x = \frac{2.1945\ t}{A}.$$

To determine the carbon dioxide in a mixture of soluble carbonates and bicarbonates, precipitate with barium or calcium chloride and titrate with normal nitric or hydrochloric acid.

If a is the amount of nitric acid in 1 cc.. t, the number of cc. of acid used, then

$$\begin{gathered} HNO_3 : CO_2 \\ 62.89 : 21{:}945 = a\ t : y \end{gathered}$$

$$y = \frac{21.945\ a\ t}{62.89}$$

$$A : \frac{21.945\ a\ t}{62.89} = 100 : x$$

$$x = \frac{100\ .\ 21.945\ a\ t}{62.89\ A} \text{ per cent. } CO_2.$$

For the analysis of carbonates which contain an indefinite amount of carbon dioxide, e. g., zinc carbonate, copper carbonate, lead carbonate, dolomite, etc., Mohr recommends the following method : Decompose the compound with an acid, absorb the evolved carbon dioxide in ammonium hydroxide in a suitable apparatus, add barium or calcium chloride and then determine the carbon dioxide in the precipitate, with normal nitric or hydrochloric acid. It is much simpler and better. however, to determine the carbon dioxide by determining the loss which the carbonate suffers when treated with an acid.

Determination of Free Carbon Dioxide absorbed in Water, and of Carbon Dioxide in Mineral Waters :—Fill an accurately calibrated pipette, of about 500 cc. capacity, with the water, transfer to an ammoniacal solution of barium chloride, and rinse out the pipette with distilled water. Filter out the precipitate of barium carbonate, wash with water, and titrate with normal nitric or hydrochloric acid.

Determination of the Alkaline Earths :—To determine the amount of barium in a water, first determine the specific gravity of the solution, draw off a few cc. with a pipette, add an indicator and titrate with normal hydrochloric or nitric acid.

To determine barium in its soluble salts, dissolve a weighed sample in water, add ammonium hydroxide and ammonium carbonate and heat to boiling. Filter out the precipitate of barium carbonate and wash with hot water by decantation, until the filtrate does not show an alkaline reaction. Suspend the precipitate in water and titrate with normal acid.

1 Eq. of nitric acid HNO_3, = 62.89 grams, corresponds to 1 Eq. of BaO, = 76.41 grams ; or, 1 Eq. of $BaCO_3$, = 98.355 grams.

If t represents the number of cubic centimeters of normal nitric acid used, and a the amount of HNO_3, in 1 cc., then the following proportion is obtained, e. g., for barium carbonate :

$$62.89 : 98.355 = a\ t : x.$$

The determination of strontium and calcium is similar to that of barium.

ACIDIMETRY.

DETERMINATION OF ACIDS.

Acids and acid-reacting salts may be determined by titration with an alkali of known concentration. Add an indicator to the solution of a weighed sample (see Alkalimetry), and titrate with a normal alkali, to the end reaction. Normal potassium or ammonium hydroxide may be used. The necessary directions for the preparation of the standard solutions have been given above.

If

M, represents the equivalent weight of the acid being determined,

A, the weight of acid taken for analysis,

t, the number of cc. of normal ammonium hydroxide used in the titration, and

a, the amount of NH_3 in 1 cc.,

then

$$17.01 : M = a\,t : y\,;$$

$$y = \frac{M\,.\,a\,t}{17.01}\,.$$

$$A : \frac{M\,.\,a\,t}{17.01} = 100 : x\,;$$

$$x = \frac{100\,.\,M\,.\,a\,t}{17.01\ A}, \text{ per cent of acid.}$$

The following acids and acid-reacting salts, may be determined according to the above principles :

	M.
Sulphuric Acid, H_2SO_4, . . .	48.91
Sulphuric Anhydride, SO_3, . .	39.93
Potassium Acid Sulphate, $KHSO_4$, .	135.85
Sodium Acid Sulphate, $NaHSO_4$, .	119.82
Hydrochloric Acid, HCl, . . .	36.37
Hydrobromic Acid, HBr, . .	80,76
Hydriodic Acid, HI, ...	127.54
Hydrofluoric Acid, HF, . .	20.06
Nitric Acid, HNO_3, . . .	62.89
Acetic Acid, $HC_2H_3O_2$, . . .	50.88
Oxalic Acid (*crystallized*), $H_2C_2O_4+2H_2O$,	62.85
Potassium Acid Oxalate, $KHC_2O_4+H_2O$,	145.77
Tartaric Acid (*crystallized*), $C_4H_4O_6$,	74.82
Potassium Acid Tartrate, $KHC_4H_4O_6$,	187.67
Citric Acid, $H_3C_6H_5O_7$, . . .	63.84

If several samples are to be determined, it is simpler to determine the specific gravity of the acid, and then multiply by the number of cubic centimeters of acid used, than to weigh each sample.

In analyzing crude, colored vinegars, it is not advisable to add the indicator, as the color change is not readily apparent; it is preferable to first gradually add the alkali, and then to transfer a drop of the liquid to the indicator*. If the vinegar is very much colored, it is advisable to add at once an excess of normal barium hydroxide and then titrate the excess with hydrochloric acid.

In testing crude cream of tartar, the solution assumes a green color, instead of violet, if litmus is used as indicator.

Since cream of tartar is difficultly soluble, the solution must either be heated for some time after assuming the green color, or the solution must be heated before titration.

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* In this case, use red litmus paper for the indicator.

Determination of Potassium as Potassium Acid Tartrate :—Dissolve a weighed sample of the potassium salt in water, add a solution of sodium acid tartrate and evaporate to dryness on the water-bath. Add dilute alcohol to the residue, filter off the residue of potassium acid tartrate, wash it with ice cold water and then dissolve in hot water. Titrate with a normal alkali.

Determination of Potassium or Sodium as Fluosilicate :—If an excess of fluosilicic acid is added to the solution of a potassium or sodium salt, and 1/3 the volume of alcohol added, all the potassium or sodium is precipitated as fluosilicate :

$$2KCl + H_2SiF_6 = K_2SiF_6 + 2HCl$$
$$2NaCl + H_2SiF_6 = Na_2SiF_6 + 2HCl$$

Wash the precipitate with alcohol, to remove the free acid, suspend the precipitate and filter in water, add an indicator and titrate with a normal alkali. If t cubic centimeters of normal alkali were used; (e. g., with potassium), then

$$K = 1000 : \frac{39.03}{2} = t : x;$$

$$K_2O = 1000 : \frac{47.01}{2} = t : x.$$

ANALYSIS BY OXIDATION AND REDUCTION.

The principles upon which oxidation and reduction analyses are based, are as follows :

1. Elements which are oxidizable to a higher state of oxidation, can be titrated by an oxidizing solution of known concentration.

2. Elements which are reducible, are reduced by a known excess of a reducing solution, and the excess then titrated with an oxidizing solution.

The oxidizing solutions most frequently used, are : Potassium Permanganate, Iodine, Potassium Bichromate and Potassium Ferricyanide. The common reducing solutions are : Sodium Thiosulphate,* Arsenous Acid, Sodium Arsenite, Ferrous Salts, and Stannous Chloride. When potassium permanganate is used, the end of the reaction is shown by the intense reddish violet color produced by the slightest excess of the reagent. The end reaction with iodine solution, is the blue color of iodide of starch, produced by the slightest excess of iodine in the presence of starch. By suitably using the above oxidizing and reducing reagents, many groups of methods may be derived, of which the following are the most important :

Potassium Permanganate and Ferrous Salts,
Iodine and Sodium Thiosulphate, and
Iodine and Sodium Arsenite.

Potassium Permanganate and Ferrous Salts.

The use of potassium permanganate in volumetric analysis depends upon the fact that the permanganic acid gives up 5/7 of its oxygen to easily oxidizable substances, being itself reduced to a manganous salt:

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* Bunsen used sulphurous acid.

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

If a solution of potassium permanganate is added to a solution of an oxidizable substance, the color of the permanganate disappears as long as oxidation takes place. As soon as the oxidation is complete, the slightest excess of permanganate gives a violet color to the solution.

The substances which can be determined by potassium permanganate, are mostly metals having 2 degrees of oxidation, of which the lower can be oxidized to the higher by permanganate (FeO to Fe_2O_3; Cu_2O to CuO; MnO to MnO_2, etc.). The amount of permanganate used is thus a measure of the oxygen required to oxidize the metal from the lower to the higher state of oxidation. Knowing the amount of permanganate used, it is easy to compute the amount of the lower oxide. Since the permanganate is reduced to manganous oxide, free acid must always be present to form a manganous salt. In making a titration, no substances, which reduce permanganate, other than the substance being determined, should be present. Among the substances which decompose permanganate, may be mentioned: free alkalies, hydrochloric acid in more than a very small amount, nitric acid, sulphur dioxide, hydrogen sulphide, organic acids, and other organic substances.

Since potassium permanganate slowly decomposes in solution, it is necessary to determine the strength of the solution, from time to time. The purer the salt from which the solution is prepared, the slower does it decompose, provided the solution is preserved in a closely stoppered flask. Use the commercial crystallized salt, purify it by recrystallization, and dissolve 5 grams of the salt in 1 liter of pure, distilled water. For standardizing the solution, the following substances are suitable:

1. Metallic Iron,
2. Ferrous-Ammonium Sulphate,
3. Oxalic Acid.

Standardization with Iron:—Very fine, soft piano-forte wire is the best form to use, and the iron value must be determined by accurate analysis. Dissolve 0.2–0.25 gram is dilute sulphuric acid, while passing a current of carbon dioxide through the liquid to prevent oxidation by the air. When all of the iron is in solution, add potassium permanganate from a burette, until the end reaction appears.

As seen from the above equation, 10 Eq. of iron correspond to 1 Eq. of permanganic acid, or 279.4 parts of iron = 110.66 parts permanganic acid. From this, it is easy to compute how much iron corresponds to 1 cc. of potassium permanganate.

Instead of using piano-forte wire, it is preferable to use pure, metallic iron. Dissolve about 1 gram of ferrous-ammonium sulphate, or iron alum, in a little water, add potassium oxalate until the solution is red (with ferrous salt), or green (with ferric salt), then heat and add 4–5 grams of ammonium oxalate.

Dilute the solution to 200–250 cc., and precipitate the iron by electrolysis. For this purpose, a current of about 1 amp.* is sufficient. After 1–2 hours, break the circuit, pour out the solution at once, and wash the iron adhering to the platinum dish, first with cold water and then with absolute alcohol. Dry in the air-bath at 80–90° C. for a few minutes, and weigh. Add dilute sulphuric acid to the dish, and at once add a little sodium carbonate, to prevent the oxidation of the iron*. Now add concentrated sulphuric acid until the liquid heats up, and the iron completely dissolves. Titrate the hot solution.

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* See foot note, p. 1.

Standardization with Ferrous-Ammonium Sulphate :—Mohr recommends ferrous-ammonium sulphate, instead of pure iron or oxalic acid, for standardizing permanganate. Since, however, the crystals of the salt are liable to have inclusions of hygroscopic water, this substance is not to be recommended. The salt has the composition,

$$FeSO_4 . (NH_4)_2SO_4+6H_2O,$$

and contains 1/7 of its weight of iron. If, therefore, the weight of salt taken is divided by 7, the amount of iron corresponding to the number of cc. of permanganate used, is obtained.

Standardization with Oxalic Acid :—Oxalic Acid is oxidized by potassium permanganate to carbon dioxide and water :

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4=K_2SO_4+2MnSO_4+10CO_2 +8H_2O.$$

Normal oxalic acid may be used, or an arbitrary amount of crystallized oxalic acid may be dissolved in water ; add sufficient sulphuric acid to the solution to warm it, and then add potassium permanganate from the burette. At first, no change in the color of the permanganate will be noticed, but the reaction gradually begins, and the red color disappears. The reaction is more rapid, if considerable oxalic acid is used; finally, the characteristic pink color of the end reaction, remains permanent.

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* [It is preferable to deposit the iron on a cylindrical electrode, as described in the electrolytic determination of copper, under Chalcopyrite; the cylinder can then be trensferred to a flask, and the iron dissolved in an atmosphere of carbon dioxide.]

W. Hampe has recommended anhydrous oxalic acid for standardizing permanganate, as it can easily be preserved in a pure state. To prepare the anhydrous acid, dry the pure, crystallized acid for considerable time at 100° C., and sublime small portions in a platinum dish, condensing the oxalic acid in a beaker. The sublimed acid crystallizes in needles, having the luster of silk. Remove the sublimate from time to time, and preserve in a bottle having a ground-glass stopper, as the acid is very hygroscopic.

In calculating the strength of the permanganate, it should be remembered that, 62.85 grams of crystallized oxalic acid ($H_2C_2O_4 . 2H_2O$) correspond to 35.91 grams of the anhydrous acid ($H_2C_2O_4$), or to 55.88 grams of iron.

Applications of Potassium Permanganate.*

CALCIUM.

Calcium may be determined volumetrically as follows: Add ammonium hydroxide to the solution containing calcium, until alkaline, precipitate the calcium with a known excess of normal oxalic acid, filter out the precipitate of calcium oxalate, and determine the excess of oxalic acid in the filtrate with permanganate. The washed calcium oxalate may also be dissolved in hydrochloric acid and the oxalic acid then titrated. In the latter case, manganous sulphate must be added, to prevent the action of hydrochloric acid on permanganate. See page 111, note ‡.

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* The determination of iron in minerals, manganese dioxide in pyrolusite, manganese in iron ores, and of organic matter, has been given in various places. See: Siderite, Pyrolusite, and analysis of Well Water.

1 Eq. of Oxalic Acid corresponds to 1 Eq. of Calcium.

LEAD.

Lead may be determined in a manner analogous to that of calcium. Add a measured excess of normal oxalic acid to the solution containing lead, add ammonium hydroxide, filter, and titrate the oxalic acid in the filtrate with permanganate.

POTASSIUM FERROCYANIDE.

If potassium permanganate is added to a hydrochloric acid solution of potassium ferrocyanide, the latter is oxidixed to ferricyanide :

$$10K_4Fe(CN)_6 + 2KMnO_4 + 16HCl = 10K_3Fe(CN)_6 + 12KCl + 2MnCl_2 + 8H_2O.$$

Dissolve the potassium ferrocyanide in water, dilute until there is about 0.1 gram of the salt in 100 cc. of solution, and acidify strongly with hydrochloric acid. Titrate with permanganate, while stirring. It is best to use a dish of white porcelain. On adding the hydrochloric acid, the solution becomes cloudy and has a slight bluish tint. The potassium ferricyanide formed, has a yellowish green color, which makes the color of the permanganate somewhat uncertain.

From the volume of permanganate used, first compute the equivalent amount of metallic iron, and from that the amount of potassium ferrocyanide.

1 Eq. of iron corresponds to 1 Eq. of potassium ferrocyanide.

If the solution contains other substances which react with permanganate, add ferric chloride to the acidified solution, filter, and wash the precipitate. Decompose the precipitate with potassium hydroxide, avoiding an excess; acidify the solution with hydrochloric acid, and then titrate with permanganate.

NITRIC ACID.

Heat a sample of the nitrate with a known excess of metallic iron, and hydrochloric acid. The iron dissolves to form ferrous chloride, and a portion is oxidized by the nitrate to ferric chloride:

$$6FeCl_2 + 2HNO_3 + 6HCl = 3Fe_2Cl_6 + 2NO + 4H_2O.$$

The excess of ferrous chloride may be titrated with permanganate.

HYDROGEN SULPHIDE.

If water containing hydrogen sulphide, is added to a solution of ferric chloride, sulphur is precipitated, and an amount of ferrous chloride equivalent to the hydrogen sulphide, is formed:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

The amount of ferrous chloride formed may be determined with permanganate.

CHROMIC ACID.

Chromic acid reacts with ferrous salts, in acid solution, to form the corresponding ferric salt and chromic salt:

$$2CrO_3 + 6FeO + 12H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 12H_2O.$$

Therefore, if a weighed excess of a ferrous salt (e. g. ferrous-ammonium sulphate) is added to a solution containing chromic acid, 6 Eq. of ferrous iron will be oxidized, for each 2 Eq. of chromic acid present. The excess of ferrous iron may be titrated with permanganate.

DETERMINATION OF FERRIC SALTS WITH STANNOUS CHLORIDE.

The determination is based upon the following reaction between ferric chloride and stannous chloride:

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

The determination may be made either by adding exactly enough stannous chloride for the reduction, or by adding an excess of stannous chloride, and then titrating the excess with iodine solution:

$$SnCl_2 + 2I + 2HCl = SnCl_4 + 2HI.$$

By adding starch solution before making the titration, the blue iodide of starch color will appear when the stannous chloride has been oxidized to stannic chloride.

The following solutions are necessary for the titration:

1. A solution of ferric chloride of definite strength. It is prepared by dissolving 10 grams of pure iron in hydrochloric acid, and then oxidizing the ferrous iron with powdered potassium chlorate. Boil the solution until all the chlorine is expelled; cool, and dilute to 1 liter.

Instead of the iron, a corresponding amount of pure ferric oxide* may be dissolved in hydrochloric acid, and diluted to 1 liter.

A weighed amount of ferrous-ammonium sulphate may also be used, and the solution oxidized with hydrogen peroxide. Expel the excess of the latter, by heating the solution.

2. Dissolve about 15 grams of tin in hydrochloric acid, and dilute to 1 liter.

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* Obtained by igniting ferrous oxalate.

3. A solution of iodine in potassium iodide. This is prepared by dissolving about 5 grams of iodine in potassium iodide, and diluting to 1 liter.

Determine the relation of the stannous chloride to the iodine as follows: Measure out about 2 cc. of the stannous chloride solution, add a few drops of starch solution and then add iodine from a burette until the solution becomes blue. Note the number of cc. of iodine used.

To determine the relation between the stannous chloride solution and the ferric chloride solution, measure out 10 cc. of the latter in a small flask, add a little hydrochloric acid, heat to boiling and add stannous chloride until the yellow color of the ferric chloride has disappeared. Cool the solution in a current of carbon dioxide, add starch solution, and titrate the excess of stannous chloride with iodine.

Since the relation of the stannous chloride to the iodine has previously been determined, the amount of stannous chloride used in reducing the ferric chloride may be obtained by subtracting from the volume of stannous chloride used, the volume of stannous chloride equivalent to the volume of iodine used.

The use of iodine may be avoided, as follows: Transfer the solution to be reduced to a large flask, and add an excess of hydrochloric acid (about 25 cc. of acid to each 10 cc. of the solution). Heat to boiling, and add the stannous chloride, drop by drop, until the solution is decolorized.

As stannous chloride slowly oxidizes, the strength must always be determined before using. To protect the solution from oxidation, place a layer of petroleum about

1 cm. thick on the surface (Mohr). A convenient flask in which to preserve the solution, is shown in Fig. 77.

Stannous chloride may be protected from oxidation by connecting a tube filled with pumice stone saturated with potassium pyrogallate, with the upper opening in the flask. The flask may also be connected with a tap on the gas main.

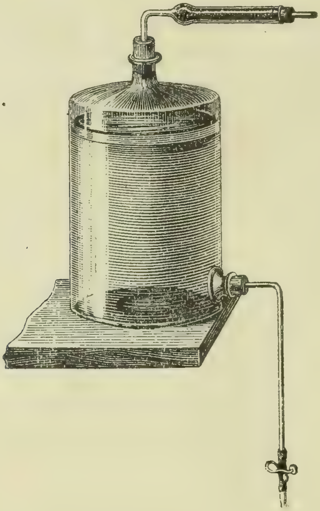

Fig. 77.

SODIUM THIOSUPHATE AND IODINE.

Crystallized sodium thiosulphate has the composition $Na_2S_2O_3+5H_2O$. When a solution of iodine in potassium iodide is added to a solution of sodium thiosulphate, the latter is oxidized to sodium tetrathionate:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

The yellow color of the iodine disappears at once when added to the thiosulphate. If starch solution* has previously been added, the solution remains colorless until all of the thiosulphate has been oxidized to tetrathionate. When the reaction is complete, one drop of iodine in excess produces the blue color.

Preparation of the Sodium Thiosulphate Solution:—Since 1 molecule of sodium thiosulphate is equivalent to 1 atom of iodine, to prepare an N/10 solution, dissolve 24.76 grams of pure, crystallized sodium thiosulphate in 1 liter of water.

Preparation of the Iodine Solution:—To prepare an N/10 solution of iodine, dissolve 12.654 grams of pure, dry iodine in a strong solution of about 20 grams of potassium iodide (free from iodate), and dilute 1 liter.

First test the sodium thiosulphate against the iodine, by measuring out 10–20 cc. of the former, adding starch solution, and then adding iodine, drop by drop, until the solution becomes blue; 1 cc. of the iodine solution must correspond to 1 cc. of the thiosulphate solution.

The thiosulphate must be standardized each time before using. For this purpose, use pure iodine, or pure potassium bichromate.

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* See note on p. 411.

Weigh out a quantity of iodine, in a closely stoppered bottle (see page 7), and dissolve in a solution of potassium iodide (1:10). Add enough of the sodium thiosulphate to decolorize the iodine. Titrate the excess of thiosulphate, with iodine, as usual.

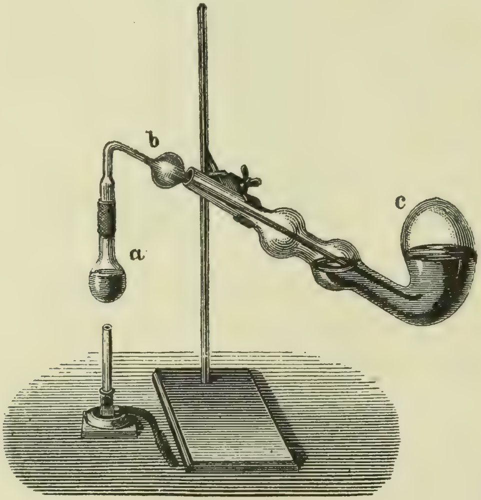

Fig. 78.

The standardization of the thiosulphate solution with potassium bichromate is based upon the fact that the latter salt, when boiled with concentrated hydrochloric acid, liberates 6 atoms of chlorine, and that the 6 atoms of chlorine liberate an equal number of iodine atoms from potassium iodide:

$$K_2Cr_2O_7 + 14HCl = 6Cl + Cr_2Cl_6 + 2KCl + 7H_2O$$
$$6KI + 6Cl = 6I + 6KCl.$$

294.68 grams of $K_2Cr_2O_7$, therefore, correspond to 759.24 grams of iodine, and 1 atom of iodine (126.54) corresponds to one molecule of sodium thiosulphate (247.6).

To make the titration, use the apparatus devised by Bunsen, Fig. 78.

a is a small flask of about 50 cc. capacity, which is connected with the pipette-shaped tube b, for carrying the vapors over into c. The tube b is drawn out to a small opening and bent upward, at its lower end. The retort c is filled 1/3 full with potassium iodine solution (1 :10).

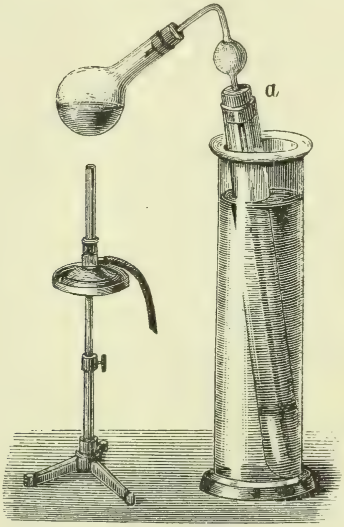

Fig. 79.

Place the weighed sample of the pulverized and dried potassium bichromate (about .05 gram) in the flask a, fill the latter about 2/3 full with concentrated hydrochloric acid, quickly connect a with b, and introduce the tube b into c. When the flask is warmed, the evolution of chlorine begins, and after boiling for a few minutes (about 1/3 of the liquid must be distilled over), all the chlorine will be expelled. Now hold the tube b with the left hand and remove it from the liquid in the flask, while heating the flask a with the right hand. When the contents of the retort are cool, rinse the liquid into a beaker, add a measured excess of sodium thiosulphate and titrate the excess with iodine.

It is now only necessary to determine the relation between the iodine and the sodium thiosulphate, to obtain the actual amount of sodium thiosulphate.

For the distillation, Mohr used the apparatus shown in Fig. 79.

Immerse the tube carrying the vapors into a glass tube 32–34 cm. long and 2.5–3 cm. wide, partly filled with potassium iodide; the tube containing the potassium iodide should stand in a larger cylinder filled with water. The stopper at a, should be inserted loosely.

When the distillation is ended, grasp the tube at a, and quickly remove from the solution.

Applications of the Method.

SODIUM THIOSULPHATE.

With an iodine solution of known concentration, it is a simple matter to determine the amount of sodium thiosulphate in a sample of impure sodium thiosulphate, or in a solution of this salt of any concentration.

If a represents the amount of iodine in 1 cc. of the iodine solution, and t the number of cc. of iodine solution used, then

$$2I : 2Na_2S_2O_3 = a\ t : x.$$

IODINE.

Instead of titrating sodium thiosulphate with iodine, the reverse process may be used, using a solution of thiosulphate which has been standardized against potassium bichromate or iodine.

If t cc. of the solution were used and if 1 cc. corresponds to a grams of iodine, the sample contains a t grams of iodine.

If A grams of the substance were used for analysis, the percentage content of iodine, therefore, is

$$\frac{100\ a\ t}{A}.$$

CHLORINE.

To determine the content of free chlorine in a solution, pour a measured quantity of it into an excess of potassium iodide solution; an equivalent amount of iodine is liberated. Now add starch solution, and titrate until the blue color disappears, or add an excess of thiosulphate and then titrate the excess with standard iodine.

$$2Na_2S_2O_3 : 2Cl = a\ t : x$$

$$x = \frac{Cl}{I}\ a\ t.$$

BROMINE.

Pass the bromine into potassium iodide solution, and proceed as given above.

CHLORINE AND IODINE.

To determine chlorine and iodine in a mixture, or in a compound, measure out 2 equal volumes of the solution. Decolorize one half with sulphuric dioxide, and precipitate with silver nitrate.

Let A represent the weight of the precipitate of silver chloride and silver iodide.

In the other half of the solution, determine with thiosulphate the amount of iodine, a t, which is equivalent to the chlorine and iodine.

From the 2 experiments, the following equations are obtained :

$$\frac{AgCl}{Cl} x + \frac{AgI}{I} y = A \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$\frac{I}{Cl} x + y = a\ t \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$x = \frac{A - \frac{AgI}{I} a\ t}{\frac{AgCl}{Cl} - \frac{AgI}{I}} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The preceding method is not applicable, if the solution contains compounds of chlorine other than the one being determined.

It is more convenient to precipitate the iodine as palladous iodide, in one half of the solution, and then ignite to metallic palladium (p) :

$$Pd : I_2 = p : y$$

$$y = \frac{I_2}{Pd} p.$$

If this value for y is substituted in equation (2) above, the following is obtained :

$$\frac{I}{Cl} x + \frac{I_2}{Pd} p = a\ t.$$

From which,

$$x = \frac{a\,t - \frac{I_2}{Pd}\,p}{\frac{I}{Cl}};$$

or,

$$x = \frac{Cl}{I}\,a\,t - \frac{Cl_2}{Pd}\,p.$$

CHLORINE AND BROMINE.

To determine chlorine and bromine, dissolve the sample in potassium iodide solution, and titrate the liberated iodine with thiosulphate.

If x = the quantity of bromine, and
y = the quantity of chlorine,

then,

$$x + y = A$$

$$\frac{I}{Br}\,x + \frac{I}{Cl}\,y = a\,t$$

$$x = \frac{a\,t - A\,\frac{I}{Cl}}{\frac{I}{Br} - \frac{I}{Cl}}.$$

DETERMINATION OF CHLORITES AND HYPOCHLORITES.

Hypochlorous acid, when treated with hydrochloric acid and potassium iodide, liberates 4 atoms of iodine :

$$Cl_2O + 2HCl + 4KI = 4KCl + 4I + H_2O.$$

Chlorous acid, under the same conditions, liberates 8 atoms of iodine :

$$Cl_2O_3 + 6HCl + 8KI = 8KCl + 8I + 3H_2O$$

To make the determination, dissolve the salts in water, add potassium iodide, and then add hydrochloric acid to acid reaction.

If A represents the weight of the sample taken, and t cc. of thiosulphate solution were used, of which each cc. = a grams of iodine, then

$$\frac{100\ Cl_2O}{4\ I\ .\ A}\ a\ t, = \text{per cent. hypochlorous acid, and}$$

$$\frac{100\ Cl_2O_3}{8\ I\ .\ A}\ a\ t, = \text{per cent. chlorous acid.}$$

The same method is also applicable to the technical valuation of chloride of lime. If enough of a solution of chloride of lime is used to correspond to the weight $\frac{100\ Cl}{I}$ the quantity a t gives the content of chlorine in per cent*.

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* The active (bleaching) constituent of chloride of lime is calcium hypochlorite, $Ca(OCl)_2$. The bleaching effect depends upon the fact that this compound, when treated with hydrochloric acid, liberates chlorine:

$$Ca(OCl)_2 + 4HCl = Ca\ Cl_2 + 2H_2O + 4Cl.$$

The valuation of chloride of lime therefore consists in the determination of the liberated chlorine; the valuation of chloride of lime may also be based upon the equation given above under Hypochlorous Acid, by determining the equivalent amount of iodine liberated by the chlorine.

The calculation is given in the following proportions:

$4\ I : 4\ Cl = a\ t : x\ ;\ x = \frac{Cl}{I}\ a\ t$, parts by weight of active chlorine in A grams of the substance. $A : \frac{Cl}{I}\ a\ t = 100 : x\ ;\ x = \frac{100\ Cl}{I\ .\ A}\ a\ t$, per cent. of active chlorine.

From the last formula, it follows that the quantity $A = \frac{100\ Cl}{I}$ must be weighed out, so that, as indicated above, the per cent. of active chlorine shall be obtained direct from the quantity a t.

CHROMATES.

As mentioned on page 438, chromates, when boiled with an excess of concentrated hydrochloric acid, evolve a definite amount of chlorine. If the chlorine is passed into a solution of potassium iodide, an equivalent amount of iodine is liberated, and may be titrated with thiosulphate. The amount of chromic acid in the sample A, is obtained from the equation :

$$x = \frac{2CrO_3}{6\ I}\ a\ t,$$

or, in per cent.,

$$x = \frac{200\ CrO_3}{A\ .\ 6\ I}\ a\ t.$$

If A is made equal to $\frac{200\ CrO_3}{6\ I}$, i. e., if this amount is weighed out for analysis, the quantity a t gives the per cent. of chromic acid direct. In a similar manner, a t will give the per cent. of potassium bichromate or lead chromate, if

$$A = \frac{100\ K_2Cr_2O_7}{6\ I},\ \text{or}$$

$$A = \frac{200\ PbCrO_4}{6\ I}$$

is weighed out for analysis.

CHLORATES.

Proceed as given above. The amount of chloric acid, x, contained in t grams of the chlorate, is

$$x = \frac{100\ Cl_2O_5}{A\ .\ 12\ I}\ a\ t.$$

LEAD DIOXIDE.

Since lead dioxide reacts with hydrochloric acid as follows:

$$PbO_2 + 4HCl = PbCl_2 + 2Cl + 2H_2O,$$

2 atoms of chlorine = 2 atoms of iodine = 1 molecule of lead dioxide = 2 Eq. of oxygen. Therefore,

$$x = \frac{100\ PbO_2}{A\ .\ 2\ I}\ a\ t,$$

or, in per cent. of oxygen,

$$x = \frac{100\ O}{A\ .\ 2\ I}\ a\ t.$$

MANGANESE DIOXIDE.

Manganese dioxide, when boiled with hydrochloric acid, decomposes in a manner similar to lead dioxide. The amount of manganese dioxide in a sample A, therefore, is,

$$x = \frac{100\ MnO_2}{A\ .\ 2I}\ a\ t.$$

In a similar manner, silver peroxide, manganic oxide, ($Mn_2O_3 + 6HCl = 2MnCl_2 + 2Cl + 3H_2O$), trimanganese tetroxide ($Mn_3O_4 + 8HCl = 3MnCl_2 + 2Cl + 4H_2O$), etc., may be determined.

IODATES.

When iodic acid or an iodate is distilled with an excess of concentrated hydrochloric acid, 10 atoms of chlorine and 2 atoms of iodine are liberated:

$$2HI0_3 + 10HCl = 2I + 10Cl + 6H_2O.$$

x is therefore equal to,

$$\frac{100\ HIO_3}{A\ .\ 12\ I}\ \text{a t.}$$

COPPER

When potassium iodine is added to a cupric salt, cuprous iodine is precipitated, and an amount of iodine equal to that in the precipitate, is liberated :

$$2CuSO_4 + 4KI = Cu_2I_2 + 2I + 2K_2SO_4.$$

The liberated iodine may be titrated with sodium thiosulphate.

HYDROGEN SULPHIDE.

When iodine is added to a solution containing hydrogen sulphide, hydriodic acid is formed, and sulphur is liberated :

$$H_2S + 2I = 2HI + S.$$

If starch solution is added to a solution containing hydrogen sulphide, and iodine solution then added, the blue color of iodide of starch appears, when the above reaction is complete. The method gives good results only when the amount of hydrogen sulphide is below .04 per cent. If more hydrogen sulphide is present, the solution must be diluted with a suitable amount of boiled water.

1 cc. N/10 iodine solution = .001699 gram H_2S.

SODIUM ARSENITE AND IODINE.

CHLORIMETRY.

Iodine does not react with arsenous acid, but does react with sodium arsenite, forming sodium arsenate and hydriodic acid:

$$Na_3AsO_3 + 2I + H_2O = Na_3AsO_4 + 2HI.$$

The liberated hydriodic acid, however, reacts with the sodium arsenite, forming arsenous acid. Since the latter is not oxidized to arsenic acid by iodine, the reaction between arsenite and iodine cannot take place in a neutral solution. Sufficient sodium bicarbonate must be added to form sodium iodide with the hydriodic acid. When starch solution is added to the alkaline sodium arsenite, and iodine is added, the blue color of iodide of starch appears as soon as the sodium arsenite as oxidized to sodium arsenate.

Preparation of N/10 Sodium Arsenite:—Dissolve 4.942 grams of pure sublimed arsenous acid (As_2O_3), in a little water containing about 10 grams of sodium bicarbonate, and dilute to 1 liter.

Preparation of N/100 Iodine:—If 10 cc. of the iodine solution are to correspond to 1 cc. of the sodium arsenite solution, dissolve 1.2654 grams of iodine in a strong solution of potassium iodide, and dilute to 1 liter.

As it is difficult to prepare pure and dry iodine, the iodine solution must be standardized. Measure out 5–10 cc. of the sodium arsenite, add starch solution and ascertain how many cc. of iodine are necessary for the oxidation. If, for example, 10 cc. of sodium arsenite were used, and 98 cc. of iodine were necessary for the oxidation, the proportion,

$$98 : 10 = 1 : \frac{10}{98},$$

shows that 1 cc. of the iodine corresponds to $\frac{10}{98}$ cc. of the sodium arsenite.

Applications of the Method.

ARSENOUS ACID.

Dissolve the acid in a hot solution of an excess of sodium bicarbonate, cool, add starch solution, and titrate to the blue color with iodine. If a represents the amount of iodine in 1 cc. of the iodine solution, and t the number of cc. of the solution used, then,

$$I : \frac{As_2O_3}{4} = a\,t : x.$$

To determine the amount of As_2O_3 in commercial realgar and orpiment, dissolve a weighed sample in an excess of sodium bicarbonate, acidify with acetic acid, heat until the odor of hydrogen sulphide cannot be detected, and filter out the arsenic sulphide. Add an excess of sodium bicarbonate, cool and titrate with iodine.

IODINE.

Dissolve in potassium iodide and titrate with sodium thiosulphate. See preceding method.

$$\frac{As_2O_3}{4} : I = a\ t : x$$

BROMINE.

Bromine reacts with sodium arsenite in the same manner as iodine. A weighed sample of bromine may, therefore, be reduced with a measured excess of sodium arsenite, and the excess of the latter titrated with iodine.

CHLORINE.

To determine the content of chlorine in chlorine-water, add a measured amount of the water to a measured excess of sodium arsenite, add starch solution and titrate the excess of arsenite with iodine. Subtract the excess from the total amount used. Then,

$$\frac{As_2O_3}{4} : Cl = a\ t : x.$$

HYPOCHLOROUS ACID. CHLORIDE OF LIME.

EAU DE JAVELLE.

Commercial chloride of lime consists of calcium hypochlorite, together with calcium hydroxide, etc.

Its commercial value depends upon the content of hypochlorous acid. Hypochlorous acid reacts with sodium arsenite, as follows:

$$2Na_3AsO_3 + Ca(OCl)_2 = 2Na_3AsO_4 + CaCl_2.$$

1 mol. of hypochlorous acid corresponds to 1 mol. of arsenous acid. If .3537 gram of chloride of lime is taken for analysis, each cc. of sodium arsenite corresponds to .003537 gram of chlorine, = 1 per cent.

To make a determination, grind the sample of chloride of lime with water in a porcelain mortar, rinse into a beaker, and add an excess of sodium arsenite. A white precipitate is formed at first, which dissolves on addition of more arsenite. As long as the arsenite is not in excess, a drop of the liquid will give a blue color on potassium iodide-starch paper. Add starch paste to the cloudy solution and titrate the excess of arsenite with iodine.

Penot added only sufficient sodium arsenite to reduce the chloride of lime, and determined the end reaction by testing a drop of the solution on potassium iodide-starch paper. At first the paper is strongly blued, but as the chloride of lime is gradually reduced, the color becomes fainter, until at last it no longer appears. With a little care, it is easy to make the titration without adding an excess of arsenite. Penot's method is generally used.

Weigh out exactly 7.074 grams of chloride of lime, dissolve in water and dilute to 1000 cc. If 50 cc. of this solution are used for the titration, the number of cc. of N/10 sodium arsenite used, expresses the per cent. of active chlorine in the chloride of lime.

To prepare the potassium iodide-starch paper, stir 3 grams of starch in about 200 cc. of cold water, boil, and add 1 gram each of potassium iodide and sodium carbonate. Dilute to about 500 cc., and saturate strips of white paper with the solution.

CHROMATES.

The deportment of chromates on boiling with concentrated hydrochloric acid, has been explained above (page 438). To determine chromates, proceed as given above.

$$6Cl = 2CrO_3 = 1\tfrac{1}{2}As_2O_3.$$

Therefore,

$$1\tfrac{1}{2}As_2O_3 : 2CrO_3 = a\ t : x;$$

or, calculated to potassium bichromate:

$$6Cl = K_2Cr_2O_7 = 1\tfrac{1}{2}As_2O_3.$$

$$1\tfrac{1}{2}As_2O_3 : K_2Cr_2O_7 = a\ t : x.$$

CHLORATES.

Chlorates, when heated with concentrated hydrochloric acid behave like chromates, and liberate 6 atoms of chlorine. In the analysis of chlorates, use Bunsen's or Mohr's apparatus, and pass the chlorine into a measured excess of sodium arsenite solution. After complete decomposition, add starch and titrate the unoxidized arsenite with iodine.

$4Cl = As_2O_3$; $12Cl = 3As_2O_3$; $12Cl = Cl_2O_5$; therefore $Cl_2O_5 = 3As_2O_3$.

$$3As_2O_3 : Cl_2O_5 = a\ t : x.$$

MANGANESE DIOXIDE.

Boil a weighed sample of pyrolusite with hydrochloric acid, and pass the liberated chlorine into sodium arsenite solution.

$$MnO_2 = 2Cl\ ;\ Cl = \tfrac{1}{2}MnO_2 = \tfrac{1}{4}As_2O_3.$$

$$\tfrac{1}{2}As_2O_3 : MnO_2 = a\ t : x, \text{ or}$$

$$As_2O_3 : 2MnO_2 = a\ t : x.$$

COBALTIC OXIDE.

Cobaltic oxide, when boiled with concentrated hydrochloric acid, liberates 6 atoms of chlorine:

$$Co_2O_3 + 6HCl = 2CoCl_2 + Cl_2 + 3H_2O.$$

$$2Cl = Co_2O_3 = \tfrac{1}{2}As_2O_3\ ;\ \text{therefore,}$$

$$As_2O_3 : 2Co_2O_3 = a\ t : x.$$

HYDROGEN SULPHIDE.

To determine the content of hydrogen sulphide in a water, pipette out a quantity of the water and add to a measured excess of sodium arsenite.

If hydrochloric acid is now added in slight excess, arsenous sulphide is precipitated. Transfer the solution and precipitate to a 1/2 liter flask, fill to the mask and either siphon off 100 cc. of the clear solution, or filter 100 cc. through a dry, folded filter. Saturate with sodium bicarbonate, and titrate the excess of sodium arsentei with iodine.

Since

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.,$$
$$As_2O_3 = 3H_2S.$$

ANTIMONOUS ACID.

In alkaline solution, antimonous acid behaves like arsenous acid, and is oxidized by iodine to antimonic acid. Dissolve the antimonous acid in tartaric acid, saturate with sodium bicarbonate and titrate with iodine. Tartar emetic may be dissolved in water, sodium bicarbonate added, and the solution then titrated with iodine.

$$4I = Sb_2O_3.$$
$$4I : Sb_2O_3 = a\ t : x\ ;\ \text{or}$$
$$4\ .\ 126.54\ : 288.46 = a\ t : x.$$

For tartar emetic, the following proportion is obtained :

$$4I : 2KSbOC_4H_4O_6 = a\ t : x.$$

ANALYSIS BY PRECIPITATION.

DETERMINATION OF SILVER WITH STANDARD SODIUM CHLORIDE.

This method is based upon the precipitation of silver as silver chloride, by means of a solution of sodium chloride of known concentration. The solution should contain free nitric acid. Add the sodium chloride solution as long as silver chloride is precipitated. It may easily be seen when the precipitation is complete, by warming the solution, and shaking vigorously after each addition of salt solution; the silver chloride collects together, and the solution soon becomes clear.

Use a solution of sodium chloride containing 5.837 grams of pure sodium chloride per liter. 1 cc. of this solution corresponds to .01076 grams of silver.

DETERMINATION OF SILVER OR COPPER WITH AMMONIUM SULPHOCYANATE.

Volhard has based a volumetric determination of silver upon the following reaction:

$$AgNO_3 + NH_4SCN = AgSCN + NH_4NO_3.$$

To prepare the standard solution, dissolve about 8 grams of pure ammonium sulphocyanate in 1 liter of water. Standardize the solution against a weighed amount of pure silver, dissolved in nitric acid. Boil the solution to expel the oxides of nitrogen, cool, and titrate. Dilute with water, add a solution of ammonium-ferric sulphate, saturated in the cold (about 5 cc. to 200–300 cc. of solution), and titrate with the ammonium sulphocyanate, while constantly stirring. When all of the silver has separated as white silver sulphocyanate, the solution assumes a permanent pale red color.

Copper may be determined in a similar manner. According to Volhard, copper is precipitated as cuprous sulphocyanate, if the solution contains sulphur dioxide. Add an excess of ammonium sulphocyanate, and titrate back with a solution of silver nitrate of known concentration.

Besides the ammonium sulphocyanate solution described above, a silver solution is necessary. Dissolve 10.766 grams of C. P. silver in nitric acid, boil, to expel the oxides of nitrogen, and dilute to 1 liter. Add an excess of sulphur dioxide water to the copper solution, heat to boiling, add a measured excess of the ammonium sulphocyanate solution, cool, and dilute to a definite volume. Filter an aliquot portion of the solution, add ammonium-ferric sulphate for an indicator, and titrate the excess of ammonium sulphocyanate with silver nitrate.

DETERMINATION OF CHLORINE WITH SILVER NITRATE SOLUTION.

The determination of chlorine in soluble chlorides is based upon the same principle as the determination of silver with a solution of sodium chloride. Since, however, it is more difficult to detect the end reaction, potassium chromate (K_2CrO_4), is used for the indicator ; this substance, with silver nitrate, produces a brick red precipitate of silver chromate. If a small amount of potassium chromate is added to the solution of a chloride, so that the solution is colored a pale yellow, and silver nitrate then added, a permanent precipitate of red silver chromate forms only after all of the chlorine is precipitated as silver chloride, As silver chloride is white, it is easy to see the silver chromate. As silver chromate is easily soluble in acids, the solution must not contain any free acid.

107.66 grams of silver correspond to 35.37 grams of chlorine. Dissolve 10.766 grams of silver in nitric acid, remove the excess of acid by evaporation, dissolve the residue in water, and dilute to 1 liter. Instead of metallic silver, a corresponding amount (16.955 grams) of silver nitrate may be dissolved in a liter of water.

Ammonia, Potassium, Sodium, Alkaline or Alkaline Earth Carbonates, may be determined by forming chlorides and then titrating the chlorine with silver nitrate solution. Add hydrochloric acid, evaporate to dryness, and dissolve the residue in water.

Hydrocyanic Acid (cyanides) may also be determined with a standard silver solution. When silver nitrate is added to a cyanide solution, strongly alkaline with potassium hydroxide, a precipitate is formed ; the precipitate first formed, dissolves to form the double cyanide of potassium and silver, when more silver nitrate is added, and the solution is agitated :

$$AgNO_3 + 2KCN = AgCN \,.\, KCN + KNO_3.$$

The slightest excess of silver nitrate over that required to form the double cyanide, decomposes the latter and precipitates the normal cyanide :

$$AgCN \,.\, KCN + AgNO_3 = 2AgCN + KNO_3.$$

If a few drops of a solution of sodium chloride are added before titration, silver chloride is precipitated with the silver cyanide, which makes the end reaction sharper.

1 atom of silver corresponds to 2 molecules of cyanogen or hydrocyanic acid.

ZINC.

For the volumetric determination of zinc with sodium sulphide, see Sphalerite, page 141.

SULPHURIC ACID IN SULPHATES.

Wildenstein determines sulphuric acid in sulphates by adding an excess of standard barium chloride, and then titrating the excess with a solution of potassium chromate. Potassium chromate possesses a very strong coloring power, and the slightest excess may be detected, if the titration is made in a porcelain dish. From time to time, place a drop of the solution on a watch glass, and note whether a precipitate is formed on addition of potassium chromate.

Use a solution containing 60.88 grams (or an aliquot part) of crystallized barium chloride per liter. Make up the potassium chromate solution so that 1 cc. corresponds to 1 cc. of the barium chloride solution.

PHOSPHORIC ACID IN PHOSPHATES.

This method is based upon the precipitation of phosphoric acid by uranium acetate, in acetate acid solution. Potassium ferrocyanide is used as the indicator to show when all the phosphoric acid is precipitated as uranyl phosphate.

The following solutions are necessary :

1. A solution of uranium acetate in water. Dissolve about 38 grams of crystallized uranium acetate in water, add about 5 cc. of concentrated acetic acid, and dilute to 1 liter ; 1 cc. of this solution corresponds to approximately

.005 gram phosphoric acid.

Since basic salts precipitate from the solution on standing, the latter should not be filtered and standardized for a few days after making.

2. A solution of sodium acetate, obtained by dissolving 100 grams of sodium acetate in 900 cc. of water and 100 cc. of acetic acid, Sp. Gr. 1.04.

For the titration of alkaline phosphates, the uranium solution should be standardized against crystallized sodium phosphate. Prepare either a solution of a definite concentration, containing 10.087 grams of sodium phosphate per liter, or weigh out an arbitrary amount of the salt. For the titration of calcium phosphate (manures, superphosphates, etc.), standardize the uranium acetate against calcium phosphate. It has been found that in the titration of calcium phosphate with uranium acetate, a small amount of calcium phosphate is precipitated with the uranyl phosphate. For this reason, the same conditions must be observed in the standardization and in the actual titration. The calcium phosphate solution is obtained by dissolving 5.5 grams of dry, neutral calcium phosphate in the least amount of nitric acid necessary, and diluting with water to 1 liter. The content of phosphoric acid in this solution may be determined either by precipitating 50 cc. with ammonium molybdate solution, or by evaporating a measured amount to dryness in a platinum dish, after adding ammonium hydroxide, and then igniting the residue. The content of phosphoric acid may be calculated from the weight of calcium phosphate, $Ca_3(PO_4)_2$, obtained.

To standardize the uranium solution, add 10 cc. of the sodium acetate solution to 50 cc. of the sodium phosphate or calcium phosphate solution, and then add uranium acetate solution from a burette to the cold solution until nearly all of the phosphoric acid is precipitated as uranyl phosphate. Now boil the solution, transfer a drop to a porcelain dish and test with freshly pulverized potassium ferrocyanide. The slightest excess of uranium solution will be shown by a reddish brown coloration of the powder. When this reaction appears, read the volume of uranium solution used, and calculate the value of the solution.

In using this method for the determination of phosphoric acid in phosphates, it is necessary to observe the same conditions (dilution, etc.) in the standardization and in the actual titration. See page 160.

APPENDIX

APPENDIX

SCHEME FOR QUALITATIVE ANALYSIS.

WITH SPECIAL REFERENCE TO MINERALS, ORES, SLAGS, METALS, ALLOYS, ETC.

The separation of metals from one another, is based upon their deportment with Hydrogen Sulphide, Ammonium Sulphide, Ammonium Carbonate and Sodium Phosphate. The following distinctions may be made :

1. Metals which are precipitated from acid solution by Hydrogen Sulphide ;
2. Metals which are not precipitated from acid solution by hydrogen sulphide, but are precipitated from neutral or ammoniacal solution by Ammonium Sulphide ;
3. Metals which are not precipitated, by hydrogen sulphide or by ammonium sulphide, but are precipitated by Ammonium Carbonate ;
4. Metals which are not precipitated by the above reagents, but are precipitated by Sodium Phosphate ;
5. Metals which are not precipitated by any of these reagents.

It is possible, therefore, to divide all of the metals (also some of the acids) into 5 large Groups, by the successive use of these reagents ; the individual groups may then be examined by the use of other reagents.

Preliminary Tests.

In the examination of complex compounds, it is expedient to make a few preliminary tests on the dry substance; these tests often give a clue as to the nature of the substance, and may facilitate the special examination.

The preliminary tests include the observation of:

1. Deportment on heating in a closed tube;
2. Deportment on heating before the blowpipe on charcoal, in the oxidizing and reducing flame;
3. Deportment in the fused borax or salt of phosphorus bead;
4. Deportment with concentrated sulphuric acid; and
5. Deportment on heating on a platinum wire (Flame Coloration).

Heating in the Closed Tube.*

Place the pulverized substance in a glass tube fused together at one end (about 6 mm. wide and 8–10 cm. long), and heat.

The substance may evolve:

1. COLORLESS GASES: Carbon Dioxide, Carbon Monoxide, Oxygen, Hydrogen Sulphide, Sulphur Dioxide, Cyanogen, etc.
2. ACID VAPORS: Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrofluoric Acid.
3. AMMONIA.
4. COLORED GASES: Chlorine (yellowish green), Bromine (brownish red), Iodine (violet), Oxides of Nitrogen (yellow).

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* Most substances when heated, evolve water, which condenses on the cold walls of the tube, and makes the observation of the coatings uncertain. It is advisable, therefore. to gently warm the tube, after introducing the substance, and then to remove the moisture with a roll of filter paper.

If, on heating the original substance in the closed tube, a *yellow* coating is formed (deposition of a solid, volatile compound on the cold walls of the tube), it indicates:

Sulphur,
Arsenic Sulphide, or
Mercuric Iodide.

Arsenic sulphide dissolves on touching it with a solution of ammonium carbonate, and may be distinguished from sulphur, by its orange yellow color. If the coating is mercuric iodide, it will become red on rubbing with a glass rod.

If the resulting coating is *black* and has a metallic luster, it may be

Arsenic.
Tellurium,
Mercury. (the coating is then grayish white, and small drops of mercury may be seen with the aid of a lens),
Cadmium,
Selenium, or
Mercuric Sulphide.

Arsenic may be identified by its deportment with silver nitrate, in neutral solution (after solution in fuming nitric acid).

Tellurium solidifies on cooling.

Cadmium forms brownish yellow cadmium oxide, when heated with access of air.

Selenium and Mercuric Sulphide become red on being rubbed; selenium, when heated with access of air, evolves the odor of decaying radishes.

If the coating is *white*, it may be:

Antimony Oxide,
Arsenic Trioxide,

Mercuric Chloride,
Mercurous Chloride, or
Ammonium Chloride.

Arsenic trioxide volatilizes on heating, without previous fusion.

Antimony oxide fuses before it volatilizes.

Mercuric chloride fuses before volatilizing, and becomes yellowish red when touched with potassium hydroxide.

Mercurous chloride sublimes without fusion, and becomes black when touched with potassium hydroxide.

Ammonium chloride may be recognized by its deportment with potassium hydroxide, for which purpose, the original substance may be used.

If the substance being examined contains water, it will be deposited in little drops on the cold walls of the tube.

In the presence of non-volatile organic compounds, the assay is blackened on heating, owing to the separation of carbon. Since these compounds may interfere with the precipitation of various metals, they must be decomposed by ignition, before preceding to the special examination. In the presence of volatile compounds, e. g., mercury or arsenic, instead of decomposing the organic matter by ignition, it may be decomposed by warming with hydrochloric acid and potassium chlorate.

In the presence of some cyanogen compounds, e. g. potassium ferrocyanide, the substance becomes brown when heated in the closed tube, and cyanogen, hydrocyanic acid or ammonia, is generally evolved. These compounds should be treated as given above.

Testing Before the Blowpipe on Charcoal.

Place a small portion of the finely pulverized substance on charcoal, and heat with the blowpipe flame. If the substance detonates, it indicates a

Nitrate,
Chlorate,
Bromate, or
Iodate.

If, after heating, the substance leaves a white, unfused mass,

Alkaline Earths, and their salts,
Alumina,
Stannic Oxide,
Zinc Oxide,
Titanic Acid,
Tantalic Acid,
Niobic Acid, or
Tungstic Acid,

may be present. Moisten the residue with cobalt nitrate and heat. In the presence of Alumina, the mass becomes blue, Magnesia, flesh colored, Zinc Oxide, yellowish green, and Stannic Oxide, bluish green.

Mix a portion of the original substance with soda or potassium cyanide, and heat on charcoal in the reducing flame of the blowpipe.

In the presence of sulphates or substances containing sulphur, a yellow to red colored mass is obtained, which, when placed upon a piece of silver and moistened with water, produces a black spot (silver sulphide).

In the presence of metallic oxides, there is obtained either a metallic bead alone, a bead together with a coating or a coating alone.

Fused Metal Without a Coating.

The metal may be :

Gold,
Silver,
Copper, or
Tin.

To distinguish copper and tin, transfer the bead to an agate mortar and grind with water ; if copper is present, it may be detected by the red metallic flakes, after washing away the carbon. If the residue consists of white, ductile, metallic grains, tin may be present. Test in the copper bead as follows : Make a green copper bead by dissolving copper oxide in a bead of borax or salt of phosphorus, and add one of the small grains of metal. If the grains are tin, the bead will become brownish red and opaque, owing to reduction of CuO to Cu_2O, by the metallic tin.

Silver is soluble in dilute nitric acid, and may be precipitated with hydrochloric acid.

Gold remains behind, insoluble.

Fused Metal With a Coating.

Antimony,
Bismuth,
Lead,
Thallium,
Indium.

Antimony is mostly volatilized, the assay fumes strongly, and the resulting antimony oxide produced a dense white coating. Bismuth gives a dark yellow coating ; the metal itself is brittle.

Mix the original substance with a little potassium iodide and sulphur and heat on charcoal ; bismuth produces an easily volatile, scarlet red coating of bismuth iodide. Lead produces a yellow coating; the metallic bead is malleable. Indium gives a white coating, and thallium a yellow coating. Both metals are malleable.

UNFUSED METAL WITHOUT A COATING.

Nickel,
Cobalt,
Iron,
Tungsten,
Molybdenum,
Platinum,
(*Rhodium, Iridium, etc.*).,

These metals are almost all recognized by their deportment in the salt of phosphorus bead. On treating the washed metallic powder with dilute nitric acid, platinum (rhodium, iridium, etc.), remain unchanged, while tungsten and molybdenum form the corresponding acids.

COATING WITHOUT A METALLIC BEAD.

Zinc,
Cadmium,
Arsenic, and
Tellurium.

Zinc oxide is a non-volatile coating, yellow when hot, white when cold. The cadmium oxide coating is brownish yellow, and may be volatilized by heating with the blowpipe flame. The arsenic coating is very volatile, and on heating with the blowpipe flame, gives the odor of garlic. Tellurium gives a white coating with a reddish yellow border; on heating with the reducing flame of the blowpipe, the coating disappears.

Deportment of the Substance in the Borax Bead.

Place a small portion of the pulverized substance in the molten bead, heat first in the oxidizing flame and then in the reducing flame, and observe the colorations produced.

COLORATION IN THE OXIDIZING FLAME.

COLORLESS: *Alkaline Earths,*
Silver,
Zinc,
Tin,
Cadmium,
Molybdenum,
Tungsten,
Tantalum,
Niobium,
Titanium.

On strong saturation, the bead often appears yellowish, and become cloudy on cooling.

YELLOW: *Iron* (red when hot),
Nickel (violet when hot),
Cerium (reddish yellow when hot),
Uranium (reddish yellow when hot),
Vanadium.

GREEN: *Chromium* (red when hot).

BLUE: *Cobalt,*
Copper (green when hot).

VIOLET: *Manganese* (violet red when cold),
Didymium.

COLORATION IN THE REDUCING FLAME.

RED: *Copper* (opaque when strongly saturated),
Titanic Acid,
Tungstic Acid (blood red, with iron).

Yellow : *Tungsten,*
Molybdenum,
Vanadic Acid.
Green : *Iron,*
Chromium,
Uranium,
Vanadium.
Blue : *Cobalt.*
Gray : *Antimony,*
Nickel,
Zinc,
Silver,
Bismuth,
Cadmium,
Lead,
Tellurium (cloudy).

On long heating, the beads, with the exception of that containing niobic acid, become colorless.

Deportment in the Salt of Phosphorus Bead.

Coloration in the Oxidizing Flame.

Colorless : *Alkaline Earths,*
Silver,
Zinc,
Tin,
Cadmium,
Molybdenum,
Tungsten,
Tantalum,
Niobium,
Titanium,
Silica; remains undissolved, swims in the molten bead, and separates out on cooling (silica skeleton).

YELLOW : *Iron,*
Nickel,
Vanadium.
GREEN : *Chromium* (yellow when hot).
BLUE : *Cobalt.*
Copper (green when hot).
VIOLET : *Manganese,*
Didymium.

Coloration in the Reducing Flame.

COLORLESS : *Alumina,*
Alkaline Earths,
Tin,
Manganese,
Cerium,
Didymium.
RED : *Copper* (opaque),
Tungstic Acid,
Niobic Acid (in the presence of iron).
GREEN : *Uranium,*
Chromium (yellow when hot),
Molybdenum,
Vanadium (yellow when hot).
BLUE : *Cobalt,*
Tungstic Acid,
Niobic Acid (when weakly saturated).
VIOLET : *Titanic Acid* (yellow when hot),
Niobic Acid (violet when weakly saturated; blue when strongly saturated).
GRAY : *Antimony,*
Nickel,
Zinc,
Silver,
Bismuth,
Cadmium,

Lead,
Tellurium (cloudy).

Flame Coloration.

Moisten a small portion of the powdered substance with sulphuric or hydrochloric acid, take up in the loop of a platinum wire and heat in the lower part of the flame of a Bunsen burner.

Yellow :	*Sodium Compounds :* The color disappears if the flame is observed through a cobalt glass, or an indigo prism.
Yellowish Red :	*Calcium Compounds :* When observed through a green glass, the flame appears canary green.
Red :	*Strontium and Lithium Compounds :* The strontium flame is scarlet red; that of lithium, carmine red (best distinguished in the spectroscope).
Violet :	*Potassium, Rubidium and Caesium Compounds.*
Green :	*Barium Compounds* (yellowish green). *Thallium.* *Phosphoric Acid* (livid green). *Boric Acid* (grass green).
Blue :	*Copper Chloride* (green, after moistening with nitric acid).

Deportment With Sulphuric Acid.*

Place a sample of the pulverized substance in a test-tube, add about 3 times the volume of dilute sulphuric acid, and warm gently.

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* Testing with *concentrated* sulphuric acid allows conclusions to be drawn as to the presence of certain non-volatile organic substances; e. g. cyanides, ferrocyanides, etc. If these substancesare present, it should be known before beginning the special examination.

If effervescence is produced on adding dilute sulphuric acid, it indicates a carbonate. If hydrogen sulphide is evolved, sulphides are present; if free sulphur is deposited at the same time, a polysulphide is indicated. If sulphur is separated, with the evolution of sulphur dioxide, thiosulphates and thiocyanates are indicated.

Organic compounds are decomposed by concentrated sulphuric acid, generally with blackening (separation of carbon). Chlorides evolve hydrochloric acid gas, recognizable by its odor and by the white fumes produced when brought in contact with a glass rod moistened with ammonium hydroxide. Fluorine compounds evolve a strongly acid vapor of hydrofluoric acid, which etches glass. Silicofluorides evolve silicon tetrafluoride as well as hydrofluoric acid. The silicon tetrafluoride may be recognized by holding a moistened glass rod in the fumes; the silicon tetrafluoride is decomposed, with separation of silica. Bromides and iodides give a brownish red and violet red colored vapor, respectively, especially after addition of manganese dioxide; the iodine vapors condense on the cold walls of the tube as a black sublimate. Nitrates (with the addition of pieces of copper foil) and nitrites evolve red colored gases. Cyanides, ferrocyanides and ferricyanides evolve hydrocyanic acid, recognizable by its odor. Molybdic, tungstic, vanadic and titanic acids, will be reduced, if a piece of zinc is added to the acid solution, coloring the solution blue.

Solution of the Substance.

Before proceeding to dissolve the substance, it is necessary to finely pulverize it. This is especially necessary for the solution of substances which are difficultly attacked by solvents. First test a small portion of the substance by boiling with water in a test-tube; if the substance is insoluble, or partly soluble, use dilute and concentrated hydrochloric acid.*

If hydrochloric acid also fails, try nitric acid. When nitric acid is used for the decomposition of metallic sulphides, sulphur may separate, and a white residue may remain. Sulphur may easily be recognized by heating on a porcelain crucible cover. If the sulphur leaves a residue after burning, dissolve it in concentrated hydrochloric acid or aqua regia (mixture of 1 part nitric acid : 2–3 parts hydrochloric acid), and add the solution to the principal solution. If the sulphide leaves a white residue, after treatment with nitric acid, test a portion of it with the blowpipe on charcoal, and then dissolve it with concentrated hydrochloric acid or aqua regia.

In dissolving metals or metallic alloys, it is best to use nitric acid. If a white residue remains insoluble, it may be stannic oxide or antimony oxide (if the substance stance contains arsenic, copper or lead, the residue may contain a small amount of these metals); they may easily be recognized by their deportment before the blowpipe on charcoal. By fusing with sodium carbonate and sulphur, or by digestion with yellow ammonium sulphide, they may be brought into solution (CuS and PbS remain insoluble).

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* In the presence of silicates decomposable by acids, the silica is partly separated on warming with an acid, and after filtration, may be recognized as such, in the salt of phosphorus bead. If the presence of silica is shown, it must be completely separated before testing for the metals. Evaporate the hydrochloric acid solution of the substance to dryness, and heat the residue for some time on the water-bath. Warm the residue with a little dilute hydrochloric acid, add water, and filter. The silica obtained must be tested for purity (i. e, for the presence of other substances insoluble in hydrochloric acid). See: Special Reactions of the Individual Acids, Silicic Acid.

In the examination of complex compounds, it is advantageous to test separately, the different solutions obtained by treatment with water, hydrochloric acid, nitric acid, etc.

If neither hydrochloric acid, nitric acid or aqua regia effect decomposition of the substance, it is necessary to make special tests for insoluble or difficultly soluble substances. Among these may be mentioned: Sulphates, chiefly $BaSO_4$, $SrSO_4$ and $PbSO_4$; the latter is soluble in ammonium acetate or ammonium tartrate, and by this means may be separated from the other sulphates and from silica; insoluble silicates; fluorides, e. g. CaF_2; aluminum and chromium compounds, e. g. chrome iron ore; metallic chlorides, e. g. AgCl, also AgBr and AgI; metallic sulphides, e. g. MoS_2; ferrocyanides, e. g. Prussian blue; insoluble oxides and acids, e. g. strongly ignited ferric oxide, tin and antimony oxides, titanic, tantalic and niobic acids, and carbon.

Insoluble sulphates, silicates, ferrocyanides and some chromium compounds may be decomposed by fusion with 4 times their weight of a mixture of equal parts of potassium and sodium carbonates;* some of these compounds may also be decomposed by boiling with a concentrated solution of potassium or sodium carbonate.

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* If, for example, barium sulphate is fused with sodium carbonate and the fuse digested with water, sodium sulphate and the excess of sodium carbonate go into solution, while barium carbonate remains insoluble. The sodium sulphate may be separated from the barium carbonate by filtration, and the latter may then be dissolved in hydochloric acid, after washing with water.

If a silicate is fused with sodium carbonate, and the fuse is digested with water, the silica goes into solution as sodium silicate. The acid is always to be sought for in the aqueous extract of the fuse, and the metals in the residue.

If sodium carbonate is used for the decomposition of silicates, naturally the fused mass cannot be used for the examination for the alkalies. In this case, decompose the compound either with gaseous hydrofluoric acid, or mix the substance with ammonium acid-fluoride, and heat. This forms volatile silicon tetrafluoride, while the metals remains in the residue in the form of fluorides, and may be dissolved by warming with concentrated hydrochloric acid.

Fluorine and aluminum compounds may be decomposed by heating with concentrated sulphuric acid. The fluorides evolve hydrofluoric acid, and form the corresponding sulphates, e. g. $CaSO_4$ from CaF_2, which may then be dissolved by warming with hydrochloric acid.

Chrome iron ore, if very finely pulverized, may be decomposed by long fusion with a mixture of sodium carbonate and potassium nitrate.

Insoluble chlorides, bromides and iodides may easily be decomposed by reduction with zinc and dilute sulphuric acid.

For the decomposition of insoluble sulphides, fuse with a mixture of equal parts of sodium carbonate and sulphur. If, for example, Molybdenite is decomposed by this method, on extracting the fuse with water, the molybdenum goes into solution as sodium sulpho-molybdate.

Many insoluble oxides and acids, e. g. ferric oxide and alumina, titanic, tantalic and niobic acids, can be decomposed and rendered soluble by fusion with potassium acid sulphate. Insoluble ferric oxide may be rendered soluble by digesting for some time with warm potassium or sodium hydroxide; ferric hydroxide is formed, and may then be dissolved in concentrated hydrochloric acid, after decanting the excess of alkali*.

Carbon may be completely burned to carbon dioxide or carbon monoxide, by long ignition with access of air. Mix the carbon with copper oxide and ignite the mixture; carbon dioxide is formed, and may be recognized by passing it into lime water.

Examination of the Solutions.

TESTS FOR THE BASES.

As above mentioned, the bases, and some of the acids, may be divided into 5 different groups, by their different deportment with Hydrogen Sulphide, Ammonium Sulphide, Ammonium Carbonate and Sodium Phosphate.

The Hydrogen Sulphide group may be divided into 2 sub-groups, by treatment with ammonium sulphide; some of the first group sulphides being soluble, and others being insoluble, in that reagent.

Group I.

From acid solution, *Hydrogen Sulphide* precipitates the following as sulphides:

Lead, *black.*
Silver, *black.*
Mercury, *black.*
Bismuth, *dark brown.*
Copper, *black.*
Cadmium, *yellow.*
Palladium, *black.*
Rhodium, *black.*
Ruthenium, *black.*
Osmium, *black.*
Platinum,† *dark brown.*

Insoluble in Ammonium Sulphide.

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* Classen, Zeit. f. anal. Chem., Vol. 17, p. 182.

† Platinum sulphide is soluble in ammonium sulphide only if arsenic,

Antimony, *orange.*
Arsenic, *yellow.*
Tin (stannous), *brown.*
Tin (stannic), *yellow.*
Molybdenum, *dark brown.*
Tungsten,* *brown.*
Vanadium, *brown.*
Gold, *dark brown.*
Platinum, *dark brown.*
Iridium, *dark brown.*
Selenium, *reddish yellow.*
Tellurium, *black.*

Soluble in Ammonium Sulphide.

Group II.

From neutral or ammonical solutions, *Ammonium Sulphide* precipitates the following:

a, as Sulphides.

Zinc, *white.*
Iron, *black.*
Manganese, *flesh colored or green.*
Cobalt, *black.*
Nickel, *black.*
Uranium, (As UO_2S), *dark brown.*
Thallium, *black.*
Indium, *yellowish.*

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antimony, tin or gold are present, and the solubility increases with the amount of these metals. If arsenic, antimony, tin or gold are not present, but only those metals whose sulphides are insoluble in ammonium sulphide, no platinum sulphide will be dissolved if normal ammonium sulphide is used; if, however, the polysulphide is used, a very small amount will be dissolved. In all cases, then, where platinium is suspected, it is necessary to test the portion of the second half of the first group which is insoluble in nitric acid. See test for mercury.

* Tungsten and vanadium are not precipitated direct by hydrogen sulphide; their sulphides are precipitated only when ammonium sulphide is added to the solution, and the latter is acidified.

b, as Hydroxides.

Aluminum, *white.*
Beryllium, *white.*
Chromium, *green.*
Thorium, *white.*
Yttrium, *white.*
Erbium, *white.*
Cerium, *white.*
Lanthanum, *white.*
Didymium, *white.*
Zirconium, *white.*
Titanium, *white.*
Tantalum, *white.*
Niobium, *white.*

Besides these metals, Barium, Strontium, Calcium and Magnesium Phosphates and Oxalates will be precipitated, if the solution contains these acids.

The Alkaline Earth Borates, Arsenates and Tartrates are only partly precipitated by ammonium sulphide.

Group III.

Ammonium Carbonate precipitates as carbonates:

Barium, *white.*
Calcium, *white.*
Strontium, *white.*

Group IV.

*Sodium Phosphate** or *Sodium-Ammonium Phosphate* precipitates, as phosphate:

Magnesium, *white.*

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* It is preferable to use sodium-ammonium phosphate, as the precipitate of ammonium-magnesium phosphate then forms more rapidly.

Group V.

Not precipitated by any of these reagents :
Potassium.
Sodium.
Lithium.
Caesium,
Rubidium.
Ammonium.

In the following scheme for examining the group precipitates, it is assumed that all of the metals are present. It is evident, therefore, that if, e. g., hydrogen sulphide produces no precipitate, the same solution is to be used for the second group, etc.

When precipitating a metal with a reagent, the clear supernatant solution should always be tested for further precipitation with the same reagent.

Group I.

HYDROGEN SULPHIDE PRECIPITATE.

Acidify the solution with hydrochloric acid*, if it does not contain any free acid, and then add hydrogen sulphide until the solution smells strongly of the gas after shaking†. Filter out the precipitate, wash it with hydrogen sulphide water, and reserve the filtrate for the metals of the succeeding groups. Pour a little warm ammonium sulphide* onto the precipitate and allow it to digest for some time.† Filter and wash the residue with hydrogen sulphide water until all of the ammonium sulphide is washed out.

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* If the substance was dissolved in nitric acid or aqua regia, the solution must first be evaporated to dryness on the water-bath. Dissolve the residue in dilute hydrochloric acid.

If the substance contains lead, silver or mercury (ous), the addition of hydrochloric acid produces a white precipitate of the corresponding chlorides, which is blackened by hydrogen sulphide. On acidifying solutions which contain boric adid, silicic acid, antimonic acid, molybdic acid, tungstic acid, thallium (ous), hyposulphites and alkaline sulphides, a white precipitate may also be formed.

† If the preliminary examination showed arsenic to be present, and it is present in the arsen*ic* condition, hydrogen sulphide must be passed through the warm solution for a long time. If sulphur separates out on passing hydrogen sulphide through the solution, giving the latter a

The ammonium sulphide solution may contain the sulphides of Arsenic, Antimony, Tin, Gold, and Platinum,‡ and the residue insoluble in ammonium sulphide may contain the Sulphides of Lead, Silver, Mercury, Bismuth, Copper, Cadmium, Platinum, Osmium, Rhodium and Ruthenium§.

EXAMINATION OF THE AMMONIUM SULPHIDE SOLUTION.

Add dilute sulphuric acid to acid reaction, and warm until the hydrogen sulphide is expelled; this reprecipitates the sulphides dissolved by the ammonium sulphide.‖

If the precipitate is pure white (milky), it is liberated sulphur; in this case, none of the above mentioned metals can be in solution.¶ If the precipitate is yellow, orange

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milky appearance, ferric salts, manganic salts, permanganic acid or chromic acid, are indicated.

* It is better to spread out the filter in a small porcelain dish and remove the precipitate, and then digest with ammonium sulphide in the dish. If the preliminary test has not shown arsenic, antimony, etc., to be present, a small portion of the precipitate may be tested with ammonium sulphide in a test tube.

† For the detection of a small amount of copper, potassium sulphide should be used, as cuprous sulphide is somewhat soluble in ammonium sulphide.

‡ With reference to platinum sulphide, see note, p. 478. Besides the metals mentioned, the sulphides of molybdenum, tungsten, vanadium, iridium and tellurium are soluble in ammonium sulphide; their detection is given below. See: Qualitative Separation of the Rare Elements.

§ The detection of platinum and the platinum metals, is likewise given below. See preceding note.

‖ If the precipitate is dark colored, it may be copper sulphide, if ammonium sulphide was used; the dark color may also indicate platinum, gold, molybdenum, etc.

¶ To detect traces of these metals, the white precipitate must be examined more minutely.

or dark colored, filter, wash and warm gently with a concentrated solution of ammonium carbonate, to which has been added a little ammonium hydroxide.

The sulphide of arsenic is dissolved, and the sulphides of antimony, tin, etc., remain insoluble.

To prove the presence of arsenic, acidify the ammonium carbonate solution with hydrochloric acid, add hydrogen sulphide water, and warm. Filter out the precipitated arsenic sulphide, dissolve it in concentrated hydrochloric acid, with the addition of a little potassium chlorate, and add an excess ef ammonium hydroxide. Filter, if necessary, and precipitate the arsenic acid with magnesium chloride solution. The arsenic may also be detected as follows: Dissolve the sulphide in a little ammonium hydroxide, evaporate to dryness with potassium cyanide and sodium carbonate, and then heat in a closed tube; arsenic, if present, will be deposited on the cold walls of the tube in the form of a dark mirror. To detect traces of arsenic, use the Marsh test. In using this test, however, it is necessary to use a sulphate solution; this may be obtained by dissolving the arsenic sulphide in hydrochloric acid and potassium chlorate and then adding dilute sulphuric acid.

Test the residue insoluble in ammonium sulphide, either before the blowpipe on charcoal (See Preliminary Tests), or dissolve it in hydrochloric acid with the addition of a little potassium chlorate, evaporate to dryness, dissolve in dilute sulphuric acid, and test by Marsh's test. Arsine is formed, which, when ignited, deposits metallic arsenic on a piece of cold porcelain held in the flame; tin, if present, will be deposited on the zinc. For the recognition of antimony, test the solubility of the spots in sodium hypochlorite (antimony spots *insoluble*, arsenic spots *soluble*).

To detect tin, warm the solution in the flask with metallic iron (filings or wire) to reduce the stannic chloride to stannous chloride; heat until the solution appears green. Filter, and test the filtrate with mercuric chloride (white precipitate of mercurous chloride, or gray metallic mercury).

Second Method for the Separation of Arsenic, Antimony and Tin: — Precipitate the sulphides from the ammonium sulphide solution with a dilute acid, filter, wash, and warm with concentrated hydrochloric acid. The sulphides of antimony and tin dissolve, and the sulphide of arsenic remains insoluble. To detect antimony in the presence of tin, concentrate a small portion of the solution on a platinum foil, and add a small piece of zinc. Both metals are reduced, and the metallic antimony produces a black spot on the platinum. To detect tin, reduce the rest of the solution with zinc in a test-tube; filter, wash the residue, and dissolve it in warm hydrochloric acid. Test for tin with mercuric chloride, as given above.

To detect arsenic in the residue insoluble in concentrated hydrochloric acid, the method given above may be used.

To ascertain whether the arsenic was present in the arsen*ous* or arsen*ic* state, the deportment of the two with magnesium chloride, in the presence of ammonium chloride and ammonium hydroxide, may be used; arsenic acid produces a white, crystalline precipitate, while arsenous acid produces no precipitate. If both acids are present, the arsenous acid may be precipitated with hydrogen sulphide in the filtrate from the ammonium-magnesium phosphate.

To decide whether the tin was present in the original compound in the stann*ous* or stann*ic* state, test the solution with mercuric chloride. Stannous chloride produces a white precipitate, while stannic chloride gives no precipitate. Stannic tin also gives yellow stannic sulphide, which is soluble in ammonium hydroxide, while stannous tin gives brown stannous sulphide, insoluble in ammonium hydroxide.

Gold and platinum may be tested for as follows: Dissolve the sulphides in aqua regia, evaporate nearly to dryness, dissolve in water and a few drops of hydrochloric acid and precipitate the platinum as ammonium-platinic chloric with ammonium chloride. Very small quantities of platinum may be detected with potassium iodide. Add an excess of the salt to the platinum solution; very small amounts give a dark red color, and a dark rose red color is produced with but traces (.0001 gram platinum). Precipitate the gold in the filtrate from the platinum, with oxalic acid, ferrous sulphate or hydroxylamine hydrochloride.

EXAMINATION OF THE RESIDUE INSOLUBLE IN AMMONIUM SULPHIDE.

Warm the residue with nitric acid. If a portion remains undissolved,* it should be tested for mercury. Dissolve it in aqua regia, completely remove the latter by evaporation, dissolve the residue in water, filter out the sulphur and add sodium hydroxide until a precipitate just forms. Dissolve the precipitate in the least amount of hydrochloric acid necessary, and add a dilute solution of potassium iodide, drop by drop. If mercury is present, a red precipitate of mercuric iodide is formed, soluble in an excess of potassium iodide. The dry residue from the aqua regia solution may also be tested with stannous chloride. White or gray precipitate.*

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* If the residue is not treated long enough with nitric acid, a dark residue of sulphides mixed with sulphur, may remain. If the residue is yellow or gray, it is sulphur; a white, purverulent residue indicates lead sulphate The latter is soluble in warm ammonium acetate or tartrate. Under certain conditions, the residue insoluble in nitric acid may contain platinum sulphide, (See note p. 478). If platinum is suspected, roast a portion of the sulphide, which leaves metallic platinum. Dissolve in aqua regia. and proceed as given above.

Add ammonium hydroxide to the nitric acid solution of the residue that was insoluble in ammonium sulphide, until alkaline, and then add dilute sulphuric acid, whether the ammonium hydroxide produced a precipitate, or not. This precipitates the lead as white sulphate. Filter out the lead sulphate, and add hydrochloric acid to the filtrate; silver, if present, produces a white, flocculent precipitate of silver chloride. Saturate the filtrate from the silver chloride with ammonium hydroxide; bismuth gives a white precipitate of bismuth hydroxide†. If it is desired to test this precipitate more minutely, filter it out, dry and ignite until the paper is burned off, mix with a little potassium iodide and sulphur, and heat with the blowpipe on charcoal. If the precipitate was bismuth hydroxide, a volatile, scarlet red coating of bismuth iodide will be obtained.

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* Whether the mercury is contained in the original solution in the mercur*ous* or mercur*ic* condition, can be ascertained with hydrochloric acid. Mercurous salts give white mercurous chloride. Mercuric salts, with stannous chloride, give a white or gray precipitate. If both forms are suspected, precipitate with hydrochloric acid, and test the filtrate for mercuric salt with stannous chloride.

For the detection of minimum amounts of mercury, the above methods are not suitable. In such a case remove the free acid by evaporation, dissolve the residue in water with the addition of a few drops of sulphuric acid and electrolize the solution. For the negative electrode use a piece of gold foil, or a piece of gold wire, clean, and free from fat. After 5–10 hours, disconnect the electrode, wash with water and alcohol, cool in a dessicator and place in a closed tube. Draw the open end out to a capillary and warm the gold; the mercury condenses in the capillary and can be recognized with a lens.

† To detect very small amounts of bismuth, add a small quantity of lead nitrate, and then add potassium iodide, to the weakly acid solution. An orange yellow to red precipitate is formed, according to the relative quantities of the lead and bismuth.

If the solution contains copper, the filtrate from the bismuth hydroxide will be blue*. To detect cadmium in the presence of copper, add potassium cyanide until the solution is docolorized, and test with hydrogen sulphide; cadmium is precipitated as yellow sulphide, while copper remains in solution.

Cadmium may also be recognized in the presence of copper by adding sodium thiosulphate to the acid (hydrochloric or sulphuric) solution, until the latter is decolorized. If the solution is now boiled for a few minutes, all the copper is precipitated as the black sulphide. The cadmium may be tested for in the filtrate, as given above.

The two metals may also be precipitated with hydrogen sulphide, and the washed precipitate then warmed with dilute (1 :5) sulphuric acid; cadmium sulphide dissolves and may be reprecipitated with hydrogen sulphide.

Group II.

AMMONIUM SULPHIDE PRECIPITATE.

Add ammonium sulphide to the original filtrate from the hydrogen sulphide precipitate, then add ammonium hydroxide in slight excess, and then add (whether the ammonium hydroxide produces a precipitate or not) ammonium sulphide, as long as a precipitate is formed, and warm.

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* As a further test for copper, acidify a portion of the solution with hydrochloric acid and then add potassium ferrocyanide; copper gives a red precipitate of copper ferrocyanide.

The precipitate may contain: Sulphides of Zinc, Iron, Manganese, Cobalt, Nickel, and Uranium; Hydroxides of Chromium and Aluminum; Phosphates or Oxalates of Barium, Strontium and Calcium; Calcium Fluoride, and Ammonium-Magnesium Phosphate.*

Filter, and wash the precipitate, transfer it to a test-tube, add a cold mixture of 1 part hydrochloric acid, and 3 parts of hydrogen sulphide water, and shake vigorously.

If a black residue remains insoluble, nickel and cobalt may be present.† Test a small portion of the residue for cobalt in the salt of phosphorus bead (page 471), A blue coloration of the bead proves the presence of cobalt. Now dissolve the precipitate in aqua regia, evaporate to dryness on the water-bath and dissolve the residue in water. First add potassium or sodium hydroxide in slight excess, dissolve the resulting precipitate in potassium cyanide, and add sodium hypochlorite or bromine-water; a black precipitate proves the presence of nickel.‡

If cobalt is not present, nickel may be detected as follows: Expel the aqua regia by evaporation, dissolve the residue in water and add sodium hydroxide. Nickel gives a green precipitate of nickelous hydroxide.

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* The compounds of barium, strontium and calcium with boric acid, arsenic acid and tartaric acid, are but partly or not at all precipitated, and are therefore not considered here. If arsenic acid is present, it will have been detected and separated in testing the hydrogen sulphide precipitate.

† If nickel is present, it is shown by the brown color of the filtrate from the nickel sulphide, especially if an excess of ammonium hydroxide and yellow ammonium sulphide were used. Acidify the solution with acetic acid, evaporate to dryness, dissolve the residue in dilute acetic acid, and collect the residual nickel sulphide on a special filter.

‡ Another method for separating nickel and cobalt, which is suitable for quantitative work, depends upon the separation of the former as cobalt-potassium nitrite. First expel the aqua regia by evaporation, dissolve the residue in a few drops of water, add potassium or sodium hydroxide in slight excess, and then dissolve the resulting precipitate in concentrated acetic acid. Add a saturated solution of potassium nitrite which has previously been acidified with acetic acid. After standing for 12 hours, filter out the cobalt-potassium nitrite, and precipitate the nickel in the filtrate by adding an excess of potassium or sodium hydroxide.

If cobalt has previously been shown to be present, nickel may be tested for as follows: Evaporate the excess of acid, neutralize with sodium carbonate, and add potassium cyanide until the precipitate dissolves; on adding bromine-water or freshly prepared sodium hypochlorite, and warming for some time, the nickel will be precipitated as a black, hydrated nickel hydroxide, while cobalt remains in solution as potassium-cobalt cyanide.

Add nitric acid to the hydrochloric acid solution of the sulphide precipitate, boil, and then cool and add bromine-water* until the solution is colored brown. Supersaturate with sodium carbonate, warm gently for a few minutes and then filter†.

The filtrate may contain: Chromium (as sodium chromate) and uranium as sodium-uranyl carbonate (pale-yellow, flocculent, $UrO_2CO_3 . 2Na_2CO_3$).

The residue may contain: Hydroxides of zinc, iron, manganese, and aluminum, alkaline earth phosphates or oxalates, calcium fluoride and magnesium-ammonium phosphate.

Acidify the filtrate with hydrochloric acid, concentrate by evaporation, add alcohol and boil to reduce chromic acid to chromic chloride. Now add an excess of sodium carbonate. If a green or grayish blue precipitate is formed, chromium is present.* Filter out the precipitate, acidify the filtrate with hydrochloric acid and add potassium ferrocyanide. A brownish red precipitate proves the presence of uranium.

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* Heating with bromine-water is for the purpose of oxidizing the chromium to chromic acid, for its separation from the other metals. If, therefore, chromium is not present, this operation may be omitted.

† If the solution contains oxalic acid, and is heated too long, or the temperature is too high, oxalic acid (as sodium oxalate) may pass into the alkaline solution, and the uranium may also be precipitated, owing to decomposition of the soluble double compound.

If the solution contains manganese, a portion of it will be oxidized to permanganic acid. and will color the filtrate red. In the subsequent test for chromium, a little manganese hydroxide will also be precipitated.

If uranium is not to be tested for, and it is only a question of testing for chromium in the presence of iron, proceed as follows : Free the solution from acid as much as possible and pour into a solution of potassium permanganate saturated with sodium carbonate. Heat to boiling, and reduce the excess of permanganate with a little alcohol. Filter out the precipitate, consisting of the hydroxides of iron, aluminum, manganese, etc. In the presence of large quantities of chromium, the filtrate will be colored strongly yellow with sodium chromate. Acidify the filtrate with hydrochloric acid, and add a freshly prepared solution of potassium iodide. Free iodine is liberated, and may be extracted by shaking out with chloroform or carbon bisulphide, and then identified. If the filtrate is not colored yellow, owing to but a small amount of chromium being present, first concentrate by evaporation, acidify, and then test the solution by transferring a drop to a small portion of starch which has previously been moistened with a fresh solution of potassium iodide. Formation of blue iodide of starch proves the presence of chromium.

Dissolve the residue of zinc, iron, etc., in the least amount of hydrochloric acid necessary, and test a small portion of the solution for phosphoric acid, with ammonium nitrate and ammonium molybdate. Phosphoric acid gives a bright yellow precipitate.

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* If the color of the precipitate is not green or grayish-blue (e. g., if it is contaminated with manganese hydroxide), fuse the precipitate with sodium carbonate and potassium nitrate, or a platinum foil. (Yellow fuse of potassium chromate.)

Test another portion of the solution for oxalic acid. For this purpose, add an excess of sodium carbonate, and boil for some time. Filter, acidify the filtrate with acetic acid, and test for oxalic acid with calcium chloride. White precipitate.

To test for fluorine, use the original, solid substance. Use either the etching test with sulphuric acid, or mix a sample of the substance with silica, transfer to a test-tube and treat with concentrated sulphuric acid. On holding a moistened glass rod over the edge of the test-tube, the silicon tetrafluoride is decomposed, and silica is deposited as a white film on the glass rod.

If neither phosphoric acid, oxalic acid, or hydrofluoric acid are present, add ammonium chloride and ammonium hydroxide to the rest of the hydrochloric acid solution, and warm. If a pure white precipitate is formed, it can be only aluminum; if the precipitate is colored red, iron is also present. To detect both metals, dissolve the precipitate in hydrochloric acid, and test a portion of the solution for iron with potassium sulphocyanate or potassium ferrocyanide. Add an access of barium hydroxide* to the rest of the solution, boil, filter off the resulting precipitate of ferric hydroxide, and precipitate the aluminum in the filtrate by boiling with ammonium chloride.

Filter out the aluminum hydroxide, acidify with acetic acid and pass hydrogen sulphide, to precipitate zinc and manganese. If a white precipitate is formed after standing for some time, it is zinc sulphide; filter it out, add ammonium hydroxide to alkaline reaction and then add a few drops of ammonium sulphide, to precipitate the manganese. A flesh colored, or green precipitate of manganous sulphide proves the presence of manganese.*

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* Barium hydroxide is preferable to potassium or sodium hydroxide, as the latter are difficult to prepare in a pure state, and generally contain silica and alumina.

If the substance contains phosphoric acid or oxalic acid, proceed as follows:

First test a small portion of the solution for iron, with potassium ferrocyanide or sulphocyanate. Dilute the rest of the solution strongly with water, add ferric chloride until the solution is colored yellow, neutralize the free acid with sodium carbonate until there is a slight precipitate. Now acidify the solution with acetic acid, stir, add solid sodium acetate (1–2 grams will be sufficient, unless an excessive amount of ferric chloride was used), and heat to boiling. The precipitate contains all of the phosphoric acid as ferric phosphate together with basic ferric acetate; if aluminum is present, it will also be precipitated as basic aluminum acetate. For the identification of aluminum, proceed as given above.

If the solution contains oxalates, they may also be pre-

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* The precipitate should be further tested by fusion on a platinum foil with sodium carbonate and potassium nitrate. (Green fuse of potassium manganate.)

If but traces of manganese are present, ammonium sulphide forms a precipitate of manganous sulphide only after standing for some time. To confirm the presence of traces of manganese, add sodium carbonate and potassium nitrate to the ammonium sulphide solution, evaporate to dryness and fuse the residue (green fuse of potassium manganate).

The manganese may be present in the original substance as manganous oxide, manganic oxide, trimanganese tetroxide, manganese peroxide, manganic acid or permanganic acid. The first 2 forms mav be distinguished by precipitation with potassium hydroxide (manganous hydroxide, white).

If the original substance is soluble in water, and evolves chlorine when warmed with hydrochloric acid, manganic oxide, trimanganese tetroxide, or manganese peroxide, is present. (These substances cannot be further distinguished qualitatively.)

Alkaline manganates are decomposed by acids, and the green color of the solution changes to red:

$$3H_2MnO_4 = H_2MnO_3 + 2HMnO_4 + H_2O.$$

Permanganic acid can be recognized by its deportment with reducing agents, e. g., sulphurous acid; the red solution is decolorized:

$$2KMnO_4 + 5H_2SO_3 = 2MnSO_4 + 2KHSO_4 + H_2SO_4 + 3H_2O.$$

cipitated with the ferric phosphate. If the preliminary test showed oxalic acid to be present, boil the iron precipitate for some time with sodium carbonate; filter, wash the precipitate with water, dissolve it in hydrochloric acid, precipitate the iron and aluminum with ammonium hydroxide, and test the filtrate for the alkaline earths, as given under **Group III.**

Acidify the filtrate from the basic iron-aluminum acetate precipitate, with acetic acid, and add hydrogen sulphide. Filter out the white precipitate of zinc sulphide, and test the filtrate for manganese with ammonium hydroxide and ammonium sulphide. The manganous sulphide may be further tested by fusion with sodium carbonate and potassium nitrate. Acidify the filtrate from the manganous sulphide with hydrochloric acid, boil until the odor of hydrogen sulphide is gone, filter out the sulphur, add ammonium hydroxide to alkaline reaction, and precipitate the alkaline earths by boiling with ammonium carbonate. Test the precipitate for barium, strontium and calcium, as given under **Group III.** Precipitate the magnesium in the filtrate from the earth carbonates, with sodium phosphate. See **Group IV.**

Second Method in the Presence of Phosphoric and Oxalic Acids:—Dissolve the residue in hydrochloric acid, and add dilute sulphuric acid and alcohol; filter out the sulphates, wash with dilute alcohol and boil for some time with a concentrated solution of sodium carbonate. The residue contains the alkaline earths as carbonates. Filter out the precipitate, wash with water and dissolve in dilute acetic acid. Test this solution as given under **Group III.**

Test the filtrate from the sulphates, for iron, aluminum, zinc, manganese and magnesium. This solution also contains the phosphoric and oxalic acids, if they are present. Expel the alcohol by boiling, and add ammonium hydroxide in excess.

The precipitate may contain iron, aluminum, and magnesium as phosphates; the filtrate may contain manganese and zinc. Boil the precipitate with barium hydroxide and filter. The filtrate contains the alumina, which may be precipitated with ammonium chloride.

Dissolve the residue insoluble in barium hydroxide in hydrochloric acid. Add ammonium hydroxide, filter out any precipitate of ferric hydroxide, and precipitate the magnesium as phosphate, with sodium phosphate.

The filtrate containing the manganese and zinc, may be examined as given above.

Group III.

Ammonium Carbonate Precipitate.

Add hydrochloric acid to the filtrate from the ammonium sulphide precipitate, to acid reaction, boil, to expel the hydrogen sulphide, and filter. Add ammonium hydroxide to alkaline reaction, then add ammonium chloride and ammonium carbonate in excess, and heat to boiling.

The precipitate may contain Barium, Strontium and Calcium Carbonates.

Filter out the precipitate, wash it with water, and dissolve in dilute acetic acid. Dilute the solution with water and add potassium chromate, drop by drop. If a yellow precipitate is formed (barium chromate), the presence of barium is indicated. Filter out the barium chromate, dilute with water, and test for strontium with dilute sulphuric acid. If strontium is present, a white precipitate of strontium sulphate will be formed*. Calcium may be tested for in the filtrate from the strontium sulphate, by neutralizing with ammonium hydroxide and adding ammonium oxalate; calcium, if present, separates as white calcium oxalate, insoluble in acetic acid.

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* To detect traces of strontium, the solution must be allowed to stand for some time.

Second Method:—The following method may also be used for testing for barium, strontium and calcium. Precipitate the alkaline earths with ammonium carbonate, dissolve the precipitate in hydrochloric acid, evaporate to dryness and extract the residue with absolute alcohol. Barium, if present, remains insoluble as barium chloride, and after filtering and washing with absolute alcohol, may be further tested. The alcoholic solution contains strontium and calcium chlorides. Evaporate to dryness, add concentrated nitric acid to the residue, and evaporate again, to form nitrates. Extract the residue with absolute alcohol; strontium nitrate remains insoluble and may be filtered out, washed with absolute alcohol and further tested (e. g., flame coloration). Expel the alcohol from the filtrate, dissolve the residue in water, and test for calcium with ammonium oxalate, as given above.

Group IV.

Test a portion of the filtrate from the carbonate precipitate of **Group III** with sodium-ammonium phosphate. If magnesium is present, a white, crystalline precipitate of Ammonium-Magnesium Phosphate will be formed. Dilute solutions must be allowed to stand for some time.

Group V.

If magnesium is present, it must be removed before testing for the alkalies.* If the solution contains sulphuric acid,* evaporate the remainder of the filtrate from **Group III** to dryness, without adding sodium phosphate, and volatilize the ammonium salts by gentle ignition. Dissolve the residue in water, add barium hydroxide to alkaline reaction, and boil. Filter out the precipitate of magnesium hydroxide and barium sulphate, and add ammonium hydroxide and ammonium carbonate, to remove the excess of barium. Filter out the barium carbonate, evaporate the filtrate to dryness, and volatilize the ammonium salts by gentle ignition. The residue contains the alkalies in the form of carbonates; add hydrochloric acid and evaporate to dryness, to form chlorides.

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* The following method for separating magnesium, proposed by the author for the quantitative separation of magnesium from the alkalies (also applicable in the presence of sulphuric acid), may be used. First volatilize the ammonium salts by gentle ignition, dissolve the residue in dilute hydrochloric acid, and evaporate to dryness on the water-bath to

If the filtrate from the alkaline earth carbonates does not contain sulphuric acid, the following method for separating magnesium, may be used. Evaporate the filtrate to dryness, and expel the ammonium salts by gentle ignition. To the residue add about 4 times its weight of oxalic acid or ammonium oxalate, and re-ignite. This forms magnesium oxalate, which is ignited to magnesium carbonate and then to magnesium oxide, while the alkalies remain as carbonates. Digest with water, filter out the insoluble magnesium oxide, add a little hydrochloric acid to the filtrate and evaporate to dryness. The residue contains chlorides of the alkalies.

If no magnesium is present, evaporate the filtrate

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expel the free acid. Dissolve the salts in about 25 cc. of water, add an equal volume of ammonium oxalate, heat to boiling, and add an excess of concentrated acetic acid. This precipitates all of the magnesium as crystalline magnesium oxalate. If but a small amount of magnesium is present, the precipitate forms only after some time. In all cases, the liquid should be allowed to stand in a warm place for several hours. Filter, concentrate the filtrate, and test for the alkalies.

* To test for sulphuric acid, acidify a small portion with hydrochloric acid, and add barium chloride. Sulphuric acid gives a white precipitate of barium sulphate.

from the alkaline earth carbonates to dryness, ignite gently, dissolve the residue in water with the addition of a few drops of hydrochloric acid, and evaporate to chlorides.

The residue obtained by either of the above methods, should first be tested on a platinum wire before the blowpipe or in the non-luminous gas flame. If potassium (rubidium or caesium) is present, the flame will be colored violet; lithium colors the flame carmine red, and sodium intensely yellow.

If the residue is a mixture of the alkalies, the colors peculiar to potassium and lithium will be obscured by sodium, even if the latter is present in small amount. To detect potassium in the presence of sodium, in such a case, dissolve the alkaline chlorides in a little water, and precipitate the potassium with platinic chloride and alcohol. Filter out the precipitate, evaporate the filtrate to dryness and ignite in a porcelain crucible. Dissolve the residue in water, filter, and evaporate to dryness on a watch glass. If sodium is present, small cubes of sodium chloride will crystallize out. If potassium is also present, it may be detected by observing the flame coloration through a cobalt glass, or it may be recognized in a spectroscope.

For the detection of lithium in the presence of sodium and potassium, treat the alkaline chlorides with a mixture of alcohol and ether; the lithium chloride dissolves, while the other chlorides remain insoluble. Evaporate the ether-alcohol solution to dryness, and test the residue on a platinum wire in the non-luminous gas flame (carmine red coloration), or in the spectroscope.

For the detection of caesium and rubidium in the presence of potassium, sodium or lithium, add a few drops of hydrochloric acid to the chlorides, and extract with strong alcohol; the most of the potassium and sodium chlorides remain undissolved. Evaporate the alcoholic extract to dryness, dissolve the residue in a little water and precipitate with platinic chloride. The precipitate consists of potassium, rubidium and caesium-platinic chlorides. The separation of these compounds depends upon the solubility of potassium platinic-chloride in water, Boil the precipitate repeatedly with small quantities of water, and test the residue with the spectroscope, for caesium and rubidium.

To test for ammonia, place some of the original substance in a test-tube, add sodium hydroxide and warm gently. The liberated ammonia may be recognized by its characteristic odor, as well as by the white fumes of ammonium chloride formed, when a glass rod, moistened with hydrochloric acid, is held near the mouth of the test-tube*.

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* To detect slight traces of ammonia (e. g. ammonium compounds in drinking water), a solution of potassium-mercuric iodide (Nessler's reagent), may be used. This reagent is prepared as follows: Dissolve 2 grams of potassium iodide in 5 cc. of water, warm, and add sufficient mercuric iodide so that a portion remains undissolved. After cooling, dilute with about 20 cc. of water, filter, and add 30 cc of concentrated potassium hydroxide for each 20 cc. of the filtrate. This alkaline solution, when added to a solution containing ammonium hydroxide or an ammonium salt, produces a reddish brown precipitate of nitrogen dimercuric iodide. If but very slight traces of ammonia are present, the reagent produces a yellow color.

QUALITATIVE SEPARATION OF THE RARE ELEMENTS.

As indicated on pages 479 and 482, on treating the hydrogen sulphide precipitate with ammonium sulphide, the sulphides of

Molybdenum,
Iridium,
Selenium,
Tellurium,
Tungsten*, and
Vanadium*,

may be dissolved, with the sulphides of arsenic, antimony, tin, platinum and gold, or be precipitated by acidifying the ammonium sulphide solution with dilute sulphuric acid.

To detect iridium, dissolve the iridium sulphide in aqua regia, evaporate the acid and add alcohol, which precipitates the iridium as brownish red ammonium-iridium chloride. The latter precipitate, after ignition, leaves a residue of metallic iridium. If platinum is also present, it is precipitated with the iridium, and forms metallic platinum on ignition. Treat the metals with dilute aqua regia; platinum is dissolved, and iridium remains insoluble†.

For the detection of molybdenum, first heat a small portion of the sulphide before the blowpipe is charcoal;

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* See note, page 479.

† For the separation of platinum and gold, from arsenic, antimony and tin, L. de Koninck recommends to heat the precipitate of sulphides in a current of hydrochloric acid gas; antimony and tin volatilize as chlorides, and condense in the absorption flask; arsenic volitilizes as the sulphide (mixed with sulphur), while gold and platinum remain behind. The arsenic sulphide may, therefore, be separated from antimony and tin, by filtering the solution.

molybdenum forms a yellow, crystalline coating, which appears white on cooling.

Dissolve the remainder of the molybdenum sulphide in nitric acid, and test the solution for molybdenum.*

Tellurium sulphide is changed to tellurous acid by treatment with nitric acid; on boiling the solution, the tellurous acid separates out in a crystalline form. By heating the precipitate in the reducing flame of the blowpipe on charcoal, metallic tellurium is obtained, which, like antimony, again oxidizes and forms a white coating of tellurous acid. Tellurium may also be identified by the wine red color produced when potassium cyanide is added to the aqueous solution of tellurous acid.

To detect selenium, its deportment before the blowpipe on charcoal, may be used. Selenium compounds, when heated in the reducing flame of the blowpipe, evolve the odor of decaying radishes. When selenium sulphide is treated with nitric acid, selenous acid is formed. Evaporate the nitric acid, and add sulphurous acid; selenium precipitates in the form of a bright red powder, which becomes gray if the solution is warmed.

The separation of selenium from tellurium depends upon their different deportment with potassium cyanide. When both substances are fused with potassium cyanide, and the fuse is extracted with water, double cyanides are formed, tellurium-potassium cyanide, and selenium-potassium cyanide. If a current of air is passed through the solution, tellurium is precipitated, and the selenium may be precipitated in the filtrate, by boiling for some time with dilute hydrochloric acid.

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* Evaporate the nitric acid solution to dryness, dissolve the residue in hydrochloric acid, add potassium thiocyanate and a small piece of zinc. The molybdic acid is reduced, and compounds of molybdenum with the thiocyanogen are formed, which color the solution carmine red.

Or, heat the residue from the nitric acid solution with a few drops of concentrated sulphuric acid and then add a few drops of alcohol. Molybdenium forms a lasure blue color, after cooling.

For the detection of tungsten,* oxidize the tungsten sulphide to tungstic acid, with nitric acid, and fuse the tungstic acid with sodium carbonate, which forms sodium tungstate. Dissolve the fuse in water, and add stannous chloride ; a yellow precipitate is formed, which becomes blue on heating with hydrochloric acid. If but a small amount of stungstic acid is used, test in the salt of phosphorus bead. See page 471.

To detect tungsten in the presence of tin, mix the 2 oxides with twice their weight of zinc dust, and ignite for about 15 minutes in a covered porcelain crucible. Warm the residue with dilute hydrochloric acid as long as an evolution of hydrogen takes place, and then gradually add potassium chlorate. This oxidizes the tungsten to tungstic acid, which separates out as a yellow precipitate. Dilute with water, allow to stand for 24 hours, filter, and wash the tungstic acid with dilute nitric acid. After expelling the nitric acid in the filtrate by evaporation, dissolve in hydrochloric acid and test for tin as given above.†

Tungsten and molybdenum may be separated by dissolving the sulphides in nitric acid ; the tungstic acid remains insoluble, and molybdic acid dissolves.

For the detection of vanadium, heat the sulphide with nitric acid, and evaporate to dryness. The residue contains vanadic acid. Salt of phosphorus dissolves it in the oxidizing flame, to a clear bead, which becomes a beautiful green, when heated in the reducing flame.

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* As mentioned above, tungsten and vanadium are not precipitated direct by hydrogen sulphide, and in examining the ammonium sulphide solution, it is necessary to consider these elements only when the precipitate has been digested with ammonium sulphide, or when the substance has been decomposed by direct fusion with sodium carbonate and sulphur, If this is not the case, tungsten and vanadium will be found in the filtrate from the ammonium sulphide precipitate, and may be precipitated by the addition of dilute hydrochloric acid.

† Donath u. Muellner, Oest. Zeit. f. Berg.–u. Huettenwesen, Vol 35, p. 614.

If vanadic acid is dissolved in ammonium hydroxide, and solid ammonium chloride added, ammonium vanadate separates out. This deportment of vanadium may be used for its separation from tungstic acid. Filter out the ammonium vanadate, and separate the tungstic acid in the filtrate by evaporating with hydrochloric acid.

The residue insoluble in ammonium sulphide, may contain sulphides of the following metals, as well as those considered in the systematic scheme :

Palladium,
Rhodium,
Ruthenium, and
Osmium.

Fuse the sulphides with a mixture of potassium hydroxide and potassium chlorate, and digest the fuse with water. Potassium osmiate and potassium ruthenate dissolve. Filter out the insoluble portion of the fuse and wash with water. Neutralize the filtrate exactly with nitric acid, which precipitates ruthenium oxide as a black precipitate. Add an excess of nitric acid to the filtrate and distil ; osmic acid distils over, and may then be tested for.

Ignite the residue that was insoluble in water, in a current of hydrogen, which reduced rhodium and palladium to the metallic state. Treat the 2 metals with warm aqua regia ; palladium dissolves and rhodium remains insoluble.

The ruthenium oxide precipitated with nitric acid may be further tested as follows : Dissolve the precipitate in hydrochloric acid, which gives an orange yellow colored solution. Pass hydrogen-sulphide into this solution until it is colored black, and then filter; the filtrate will have a beautiful blue color, if ruthenium is present. If potassium nitrite is added to the uranium solution, a soluble double salt is formed; now add ammonium hydroxide to alkaline reaction, and then add ammonium sulphide, which produces a carmine red solution. An excess of ammonium sulphide precipitates ruthenium sulphide.

Osmic acid is characterized especially by the chlorine-like odor that is evolved when the acid is heated with nitric acid. Osmic acid may be reduced to metallic osmium by hydrogen; the metallic osmium evolves the same odor when it is heated. When sodium sulphite is added to a solution of osmic acid, the liquid first becomes bluish violet; after further action, dark blue osmous sulphite separates out.

The rhodium obtained by reduction in hydrogen may be brought into solution by repeated fusion with potassium acid sulphate. On boiling this solution with hydrochloric acid, rhodium chloride is formed, which colors the solution rose red. If potassium hydroxide is added to the solution, no change is noticed at first, but the color soon changes to yellow, and finally a yellow precipitate separates out; the precipitate becomes black when heated with an excess of potassium hydroxide.

The best method for identifying palladium is by its deportment with potassium iodide, which precipitates palladium as black palladous iodide, even from dilute solutions. Ammonium hydroxide, when added to a solution of palladous chloride, forms a flesh red precipitate of palladio-diammonium chloride. An excess of ammonium hydroxide dissolves the precipitate, forming a brown liquid, which becomes colorless on a further addition of ammonium hydroxide.

In addition to the metals mentioned on page 488, the following metals are precipitated by *Ammonium Hydroxide* and *Ammonium Sulphide*:

a, as Sulphides.

Thallium.
Indium.

b, as Hydroxides.

Beryllium.
Thorium.
Erbium.
Yttrium.
Cerium.
Lanthanum.
Didymium.
Zirconium.
Titanium.
Tantalum.
Niobium.

For their separation, the following method may be used. Dry the precipitate, ignite gently with access of air, fuse with potassium acid sulphate, and extract the fuse repeatedly with cold water. The insoluble residue contains niobic and tantalic acids; the residue will also contain some ferric and chromic oxides, if the substance contains these elements.

Fuse the soluble residue with sodium hydroxide and potassium chlorate and extract with dilute sodium hydroxide. Chromium, if present, will form soluble potassium chromate. Filter, wash out the sodium hydroxide, and separate the sodium niobate from the sodium tantalate by repeated extraction with a dilute solution of sodium carbonate, in which the sodium tantalate is difficultly soluble.

If the portion of the fuse that was soluble in water contains iron, pass hydrogen sulphide to reduce it. Now dilute the solution largely, boil, and pass carbon dioxide, which precipitates the titanic acid. The latter may be recognized in the salt of phosphorus bead, and may also be tested by its deportment with hydrogen peroxide. Dissolve the titanic acid in hydrochloric acid, and add a solution of hydrogen peroxide; the solution is colored bright yellow to orange red, according to the amount of titanium present.*

Add nitric acid to the filtrate from the titanic acid, concentrate, and precipitate with ammonium hydroxide. Cobalt, nickel, manganese and zinc, if present, remain in solution†. The residue may contain indium, iron, chromium, uranium and the earths. Dissolve the precipitate in hydrochloric acid, and add pure, concentrated potassium hydroxide ; chromium, aluminum and beryllium dissolve, while iron, indium, uranium and the earths remain insoluble. Boil the alkaline solution, which precipitates the chromium and beryllium. Filter out the precipitate, and fuse with sodium carbonate and potassium chlorate. Extract the fuse with water, acidify with nitric acid and precipitate the beryllium with ammonium hydroxide.

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* This deportment of titanium with hydrogen peroxide in the presence of potassium hydroxide may be used direct for the detection of titanium in the presence of iron, etc. If an excess of hydrogen peroxide is added to a solution of titanium, and potassium hydroxide then added, the titanium dissolves in an excess of the precipitant. In the presence of iron, manganese, etc. their hydroxides will be precipitated, and must be separated from the alkaline solution by filtration. Acidify the filtrate with hydrochloric acid, evaporate to dryness in a porcelain dish on the water-bath, dissolve the residue in dilute hydrochloric acid and test the solution with hydrogen peroxide. If more than traces of titanium are present, the charateristic color appears on acidifying the filtrate from the iron precipitate, so that evaporation is unnecessary.

This method is also suitable for the quantitative separation of titanium from iron (A. Classen, Ber. deutsch. chem. Gesell., Vol. 21, p. 370).

† For a complete separation, it is necessary to dissolve the ammonium hydroxide precipitate in hydrochloric acid, and repeat the precipitation.

As a further test for beryllium, dissolve the precipitate in hydrochloric acid, add citric acid (to prevent the precipitation of aluminum with the beryllium), and then add ammonium phosphate in access.

Dissolve the resulting precipitate in hydrochloric acid, gradually add ammonium hydroxide until the solution has an alkaline reaction, and then heat to boiling. The voluminous, slimy precipitate of beryllium phosphate changes to ammonium-beryllium phosphate, which is beautifully crystalline, and settles quickly.

Dissolve the precipitate of iron, indium and uranium in hydrochloric acid, and add barium carbonate. After standing for 6 hours, filter out the precipitate and test for indium spectroscopically. Precipitate the excess of barium in the filtrate with dilute sulphuric acid, filter out the barium sulphate and concentrate the filtrate. Neutralize with potassium hydroxide, add solid potassium sulphate and allow to stand for 12 hours. The precipitate consists of double sulphates of zirconium*, cerium, lanthanum and didymium. Filter out the precipitate, wash it with a solution of potassium sulphate, and then treat it with dilute hydrochloric acid ; the sulphates of cerium, lanthanum and didymium dissolve, and zirconium sulphate remains undissolved. Filter out the undissolved zirconium-potassium sulphate, wash a few times with dilute hydrochloric acid, and precipitate the cerium, lanthanum and didymium with ammonium hydroxide.*

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* Bailey found that zirconium could be separated quantitatively as Zr_2O_8 with hydrogen peroxide from a sulphate solution, Ann. Chem. Pharm., Vol. 232, p. 352.

The filtrate from the potassium sulphate contains ytterbium, erbium and the remainder of the beryllium. Precipitate with ammonium hydroxide, and treat the resulting precipitate with oxalic acid ; beryllium dissolves, and erbium and ytterbium remain undissolved†.

Test for thallium and indium in the original ammonium sulphide precipitate, spectroscopically. Or, dissolve the precipitate in hydrochloric acid, reduce any iron present with sulphur dioxide, neutralize with ammonium hydroxide, and precipitate thallium with potassium iodide, as bright yellow thallous iodide. Test the precipitate for thallium in the spectroscope‡.

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* To separate cerium, dissolve the ammonium hydroxide precipitate in hydrochloric acid, neutralize the solution with sodium carbonate, add sodium acetate and an excess of sodium hypochlorite, and boil. Cerium is precipitated as cerium peroxide; lanthanum and didymium remains in solution. Precipitate the latter with ammonium oxalate, ignite the oxalates to oxides and treat with dilute nitric acid. Evaporate to dryness, and heat the residue until it fuses. On extraction with water, lanthanum is dissolved and didymium remains undissolved.

† Ignite the oxalates, dissolve the residue in nitric acid, evaporate to dryness and heat strong enough to evolve oxides of nitrogen. Boil with sufficient water to obtain a clear solution, and then allow to cool; crystals of erbium nitrate separate out. Decant off the mother liquor and treat again in the same manner. By repeatedly recrystallizing the erbium nitrate the salt may be obtained in a pure state. (Bunsen.)

‡ To separate thallium from lead, add an excess of of sodium thiosulphate so that the resulting precipitate redissolves, and then add potassium iodide. If thallium is present, a yellow precipitate of thallous iodide will be formed. Under the above conditions, no lead will be precipitated. (A. Werner.)

EXAMINATION FOR ACIDS.*

The acids, like the bases, may be divided into groups, according to their deportment with certain Group Reagents: Barium Chloride, Lead Acetate, Silver Nitrate, etc. The individual acids belonging to a given group, however, cannot be separated as the bases can. The examination for acids is much facilitated by testing the dry substance with sulphuric acid, which shows the presence of many acids.

If the examination for bases has preceded that for acids, the former gives a clue as to what acids can be present; as only those acids need be considered, which, with the bases present, form compounds that are soluble in the solvent used.

In many cases, the solution of the original substance may be used for the examination for acids, although, under certain conditions, the presence of certain bases may make the identification more difficult, or even impossible. In such cases, it is necessary to remove these metals with hydrogen sulphide, ammonium sulphide, etc., before testing for the acids.

If the substance being examined for acids is insoluble in water, fuse the fine powder with 3 or 4 times its weight of potassium-sodium carbonate, boil the fuse with water and examine the filtrate, after previous neutralization with hydrochloric, nitric or acetic acid. See also page 476.

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* [The scheme provides only for those acids that are commonly met with in minerals, ores, metallurgical products and natural waters.]

Some compounds (e. g., alkaline earth sulphates, ferrocyanides, oxalates, etc.), may be decomposed by merely boiling with a solution of sodium carbonate.

Deportment With Concentrated Sulphuric Acid.*

The substance evolves a colored gas, when heated with concentrated sulphuric acid:

Nitrous Acid.
Hydrobromic Acid.
Hydriodic Acid.

The evolved gas is colorless:

Sulphurous Acid.
Hydrogen Sulphide.
Nitric Acid.
Hydrochloric Acid.
Hydrofluoric Acid.
Carbonic Acid.

No gases are evolved:

Sulphuric Acid.
Phosphoric Acid.
Arsenic Acid.
Arsenous Acid.
Silicic Acid.
Boric Acid.
Molybdic Acid.
Tungstic Acid.
Titanic Acid.
Selenic Acid.

Deportment With Barium Chloride.

From hydrochloric or nitric acid solution, the following are precipitated:

Sulphuric Acid, *white.*
Selenic Acid, *white.*

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* As a preliminary test for carbonic acid and sulphurous acid, add dilute sulphuric acid to a portion of the dry substance, and warm.

Deportment With Calcium Chloride.

The following are precipitated:

a. From neutral solution.

Phosphoric Acid, *white.*
Boric Acid, *white.*
Arsenic Acid, *white.*
Sulphurous Acid, *white.*
Carbonic Acid, *white.*

b. From neutral, or acetic acid solution.

Sulphuric Acid, *white.*
Hydrofluoric Acid, *white.*

Deportment With Silver Nitrate.

The following are precipitated:

a. From neutral solution.

Phosphoric Acid, *yellow.*
Boric Acid, *white.*
Chromic Acid, *reddish-brown.*
Arsenous Acid, *yellow.*
Arsenic Acid, *reddish-brown.*
Sulphurous Acid, *white.*
Carbonic Acid, *white.* .

b. From acid solution.

Hydrochloric Acid, *white.*
Hydrobromic Acid, *yellowish white.*
Hydriodic Acid, *pale yellow.*
Hydrogen Sulphide, *black.*

Not precipitated by Barium Chloride, Calcium Chloride or Silver Nitrate:-

Nitric Acid.
Nitrous Acid.

Special Reactions of the Individual Acids.

Sulphuric Acid is distinguished from all other acids* by the insolubility of its barium salt in hydrochloric acid. Therefore, if barium chloride produces a white precipitate in hydrochloric acid solution, the presence of sulphuric acid is proved†.

Sulphurous Acid may be recognized by the characteristic odor, which the salts evolve when heated with dilute hydrochloric acid.

If the hydrochloric acid solution of a sulphite, or an aqueous solution of sulphurous acid is boiled with stannous chloride, hydrogen sulphide is evolved, which slowly precipitates stannic sulphide.‡

A solution of sulphurous acid, or a sulphite, also evolves hydrogen sulphide§ when treated with zinc and hydrochloric acid; the hydrogen sulphide may be recognized by its blackening or browning effect on paper saturated with lead acetate or silver nitrate.

A neutral solution of ferric chloride, when added to a neutral solution of a sulphite, produces a brownish red coloration, which disappears on boiling the solution.

When hydrogen sulphide is added to a hydrochloric acid solution of a sulphite, sulphur is separated.

The precipitate produced by silver nitrate, in a solution of sulphurous acid, becomes black after boiling the solution.

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* Selenic acid is the only other acid, which, with barium chloride, gives a white precipitate insoluble in hydrochloric acid. Barium selenate may be distinguished from barium sulphate by the fact that when boiled with concentrated hydrochloric acid, it evolves chlorine, and that sulphur dioxide precipitates red selenium from the solution.

† If the solution contains a large excess of hydrochloric acid, barium chloride itself will be precipitated in a pulverulent form when its solution is added. The precipitated barium chloride, however, cannot be mistaken for barium sulphate, as on addition of water, the precipitate entirely disappears.

‡ $3SnCl_2 + SO_2 + 6HCl = H_2S + 3SnCl_4 + 2H_2O$.

§ $SO_2 + 3Zn + 6HCl = H_2S + 3ZnCl_2 + 2H_2O$.

When the solution of a sulphite is neutralized with sodium bicarbonate, and then added to a solution of zinc sulphate to which has been added a few drops of sodium nitroferricyanide, a red coloration is produced.

Hydrogen Sulphide* is recognized principally by its deportment with lead acetate and silver nitrate, and by its odor. Most metallic sulphides are decomposed by dilute hydrochloric or sulphuric acid, with an evolution of hydrogen sulphide. Those sulphides which are not decomposable by these acids, generally are soluble in nitric acid, leaving a deposit of sulphur. If sulphides are fused with sodium carbonate on charcoal, and then placed on a bright silver surface and moistened, they form a dark spot of silver sulphide.

To detect minute traces of hydrogen sulphide, or other sulphur compounds that are soluble in water, add sodium hydroxide to the solution, and then add sodium nitroferricyanide; the above compounds produce a violet red colcoloration, which disappears after some time.

Phosphoric Acid (ortho) is precipitated from nitric acid solution, by ammonium molybdate, soluble in ammonium hydroxide.

Magnesium chloride (or sulphate), when added to a solution containing ammonium chloride and an excess of ammonium hydroxide, produces a white crystalline precipitate of ammonium-magnesium phosphate†.

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* If the substance contains free sulphur, it may be extracted with carbon bisulphide. When the latter is evaporated, the sulphur crystallizes out.

† Since arsenic acid is also precipitated by magnesium chloride, phosphoric acid cannot be tested for in the presence of arsenic acid, until the latter has been removed by precipitation with hydrogen sulphide.

Nitric Acid may be recognized by its deportment with concentrated sulphuric acid and ferrous sulphate* (brown ring test).

To detect traces of nitric acid or nitrates, the following method may be used: Dissolve a small quantity of brucine in a few drops of concentrated sulphuric acid, in a small porcelain dish, and then add a few drops of the solution to be tested. If the quantity of nitric acid is not too slight, a bright red or reddish yellow color will be imparted to the liquid.

If phenyl sulphuric acid (1 phenol : 4 conc. sulphuric acid : 2 water) is added to nitric acid or the solution of a nitrate, the liquid is colored brownish red; the color changes to yellow or green, on the addition of ammonium hydroxide. Nitrous acid reacts in a similar manner.

To detect nitric acid in the presence of nitrous acid, warm the solution with dilute sulphuric acid until the nitrous acid is expelled, and then test for nitric acid as given above.

Hydrochloric Acid or chlorides, precipitate from a solution of silver nitrate, white, flocculent silver chloride, insoluble in nitric acid, soluble in dilute ammonium hydroxide or sodium thiosulphate.

Lead acetate is precipitated white; the resulting lead chloride is soluble in much hot water, from which it crystallizes out on cooling.

When concentrated sulphuric acid is added to solid metallic chlorides, hydrochloric acid gas is evolved, recognizable by its suffocating acid odor. When a glass rod that has been moistened with ammonium hydroxide is held in the mouth of the test-tube, fumes of ammonium chloride are formed.

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* If the solution also contains bromides or iodides, this method cannot be used direct, as bromine or iodine would be liberated and produce similar color phenomena. These compounds must therefore be decomposed with hydrochloric acid and the bromine or iodine removed by shaking with carbon bisulphide or chloroform. The solution can now be used for the above test.

If a mixture of a chloride and potassium bichromate is distilled with concentrated sulphuric acid from a small tubulated retort, chromic oxychloride distils over, and forms sodium chromate, when absorbed in sodium hydroxide.

If the sodium hydroxide becomes yellow, the presence of hydrochloric acid is proved.

HYDROBROMIC ACID or bromides are precipitated yellowish white by silver nitrate. The precipitate is insoluble in nitric acid, very slightly soluble in ammonium hydroxide.

Small amounts of hydrobromic acid may be detected with chlorine water and chloroform.

If a bromide is mixed with manganese dioxide and treated with concentrated sulphuric acid, brownish red vapors of bromine appear.

HYDRIODIC ACID or iodides precipitate yellow silver iodide from silver nitrate solution, insoluble in nitric acid and ammonium hydroxide.

To detect small amounts of hydriodic acid, add potassium bichromate, dilute sulphuric acid and chloroform to the solution, and shake. The iodine is liberated and is absorbed by the chloroform, imparting a violet red color to the latter.

When manganese dioxide is added to an iodide, and the mixture then treated with concentrated sulphuric acid, iodine is liberated, and may be volatilized as a violet red vapor, by warming the mixture.

The most certain method of detecting a chloride in the presence of an iodide, is to mix with potassium bichromate and distil with concentrated sulphuric acid, as given above. Bromine may be detected in another portion of the solution by adding chlorine water, and then shaking out with chloroform.

Chlorides in the presence of iodides, may be detected as given above, by distilling with potassium bichromate and concentrated sulphuric acid. The iodine may then be detected by liberating it with potassium bichromate and dilute sulphuric acid.

To detect an iodide in the presence of bromides and chlorides, add fuming nitric acid, and shake out the liberated iodine, with chloroform.

A bromide in the presence of an iodide, may be detected by adding chloroform to the dilute solution* and then adding chlorine water until the free iodine dissolved in the chloroform is oxidized to iodic acid. The violet color of the iodine entirely disappears, and the chloroform is colored yellow or orange red, if bromine is present.

For the detection of hydrochloric, hydrobromic and hydriodic acids in the presence of hydrogen sulphide or sulphides, add ammoniacal hydrogen peroxide to the solution and boil; this oxidizes all of the sulphur to sulphuric acid.

Nitric acid may be detected in the presence of hydrobromic acid, by precipitating with silver sulphate, and testing for nitric acid in the filtrate.

HYDROFLUORIC ACID may be identified by the deportment of the dry substance with concentrated sulphuric acid and silica. Place the dry substance mixed with silica, in a test-tube, add concentrated sulphuric acid, and warm gently; silicon tetrafluoride is evolved. Hold a glass rod moistened with water, over the mouth of the test-tube; the formation of a white coating of silica, proves the presence of hydrofluoric acid.

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* If the solution has an alkaline reaction, acidify with dilute hydrochloric acid, before making the test.

The etching test for hydrofluoric acid may also be used. Place the dry substance in a small lead dish, add concentrated sulphuric acid, cover with a glass which is coated with paraffin except for a few scratches to expose the glass, and warm gently. Hydrofluoric acid, if present, will attack the exposed glass, giving it a matted appearance. The etching may be seen by warming the glass and removing the paraffin.

Silicic Acid. Silicates are characterized by their deportment in the salt of phosphorus bead. Place a small amount of the pulverized substance in the bead, and fuse. The metals are dissolved, while the silica remains undissolved, and swims about in the molten bead (skeleton of silica).

If the silicate is soluble, add hydrochloric acid, and evaporate to dryness on the water-bath. When the residue is treated with dilute hydrochloric acid, the silica remains insoluble.

If a warm solution of ammonium chloride is added to a warm aqueous solution of a silicate, the silicic acid separates at once as a white precipitate, even in very dilute solutions.

Silicates which are not decomposable by acids, may be decomposed by fusion with sodium carbonate. See page 471. Dissolve the fuse in dilute hydrochloric acid, and evaporate the solution to dryness. When the residue is warmed with dilute hydrochloric acid, the silica remains insoluble.

The silica obtained by either of the above methods should be more minutely tested by its deportment in the salt of phosphorus bead*. Silica is completely soluble in potassium hydroxide†. When silica is heated in a platinum crucible with hydrofluoric acid or acid ammonium fluoride‡, it is completely volatilized as silicon tetrafluoride.

Boric Acid. Borates, when treated with hydrochloric acid, color turmeric paper brown. If the substance is heated with concentrated sulphuric acid on a platinum wire, in the outer portion of the fusion zone of the flame of a Bunsen burner, the latter will be colored distinctly green, if the substance contains a borate.

To detect a trace of boric acid, mix the dry substance with calcium fluoride and concentrated sulphuric acid, distil from a platinum retort, and receive the distillate of boron fluoride in alcohol. When the latter is ignited, the flame has a distinct green color. The substance may also be mixed with calcium fluoride and silica (or powdered glass), and treated with concentrated sulphuric acid, in a test-tube. Pass the gas into a non-luminous gas flame, through a tube drawn out to a narrow opening. The boron fluoride will color the flame green, as given above. It is advisable to place a small piece of marble in the test-tube, as to sweep the boron fluoride over into the flame, with carbon dioxide.

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* Silicates frequently contain titanic acid, which is separated with the silica. To detect the titanic acid, heat the silica with concentrated sulphuric acid, and remove the excess of acid by heating.

† This deportment can be used to separate silica from quartz (gangue).

‡ $SiO_2 + 2NH_4FHF = SiF_4 + 2NH_3 + 2H_2O$.

Carbonic Acid. Carbon dioxide is expelled with effervescence, as a colorless or odorless gas, when its compounds are treated with another acid. If the gas is passed into lime-water, a white precipitate of calcium carbonate is formed. The calcium carbonate dissolves as calcium bicarbonate, if the gas is passed for some time, and is reprecipitated when the solution is boiled.

TABLE OF ATOMIC MASSES.

Revised by F. W. CLARKE.

Chief Chemist of the United States Geological Survey.

Revised to Sept. 1902.

Name.	Symbol.	Atomic Mass. O=16	Atomic Mass. H=1
Aluminum	Al	27.1	26.9
Antimony	Sb	120.4	119.5
Argon	A	39.96	39.6
Arsenic	As	75.0	74.45
Barium	Ba	137.40	136.4
Bismuth	Bi	208.1	206.5
Boron	*B	11.0	10.9
Bromine	Br	79.95	79.35
Cadmium	Cd	112.4	111.55
Caesium	Cs	132.9	131.9
Calcium	Ca	40.1	39.8
Carbon	C	12.0	11.9
Cerium	Ce	139.0	138.0
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.00	58.55
Columbium	†Cb	93.7	93.0
Copper	Cu	63.60	63.1
Erbium	Er	166.0	164.7
Fluorine	*F	19.05	18.9
Gadolinium	Gd	156.4	155.2
Gallium	Ga	70.0	69.5
Germanium	Ge	72.5	71.9
Glucinum	*‡G	9.1	9.0
Gold	Au	197.2	195.7
Helium	He	3.96	3.93
Hydrogen	H	1.008	1.000
Indium	In	114.0	113.1
Iodine	I	126.85	125.89
Iridium	Ir	193.1	191.7
Iron	Fe	55.9	55.5
Krypton	Kr	81.76	81.15
Lanthanum	La	138.6	137.6
Lead	Pb	206.92	205.36
Lithium	Li	7.03	6.97
Magnesium	Mg	24.3	24.1
Manganese	Mn	55.0	54.6
Mercury	Hg	200.0	198.50
Molybdenum	Mo	96.0	95.3

* Symbols sometimes given with a small letter attached: Bo, Fl, Gl.
† Sometimes called Niobium, Nb.
‡ Sometimes called Beryllium, Be.

Name.	Symbol.	Atomic Mass.	
		O=16	H=1
Neodymium	Nd	143.6	142.5
Neon	Ne	19.94	19.8
Nickel	Ni	58.70	58.25
Nitrogen	N	14.04	13.93
Osmium	Os	191.0	189.6
Oxygen	O	16.000	15.88
Palladium	Pd	107.0	106.2
Phosphorus	*P	31.0	30.75
Platinum	Pt	194.9	193.4
Potassium	K	39.11	38.82
Praseodymium	Pr	140.5	139.4
Rhodium	Rh	103.0	102.2
Rubidium	Rb	85.4	84.75
Ruthenium	Ru	101.7	100.9
Samarium	Sm	150.3 ?	149.2 ?
Scandium	Sc	44.1	43.8
Selenium	Se	79.2	78.6
Silicon	Si	28.4	28.2
Silver	Ag	107.92	107.11
Sodium	Na	23.05	22.88
Strontium	Sr	87.60	86.95
Sulphur	S	32.07	31.83
Tantalum	Ta	182.8	181.5
Tellurium	Te	127.7	126.1
Terbium	Tb	160.	158.8
Thallium	Tl	204.15	202.61
Thorium	Th	232.6 ?	230.8 ?
Thulium	Tu	170.7	169.4
Tin	Sn	119.0	118.1
Titanium	Ti	48.15	47.8
Tungsten	W	184.	182.6
Uranium	U	238.5	236.7
Vanadium	*V	51.4	51.0
Xenon	X	128.0	127.
Ytterbium	Yb	173.2	171.9
Yttrium	Yt	89.0	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.4	89.7

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* Symbols sometimes given with a small letter attached: Ph, Vd.

TABLE FOR THE CALCULATION OF THE "DEGREE OF HARDNESS" FROM THE NUMBER OF CUBIC CENTIMETRES OF SOAP SOLUTION USED.

Volume of Soap Solution Used.	*Degree of Hardness*
3.4 cc.	0.5
5.4 cc.	1.0
7.4 cc.	1.5
9.4 cc.	2.0
The difference of 1 cc. of the soap solution=0.25.	
11.3 cc.	2.5
13.2 cc.	3.0
15.1 cc.	3.5
17.0 cc.	4.0
18.9 cc.	4.5
20.8 cc.	5.0
The difference of 1 cc. of the soap solution=0.26.	
22.6 cc.	5.5
24.4 cc.	6.0
26.2 cc.	6.5
28.0 cc.	7.0
29.8 cc.	7.5
31.6 cc.	8.0
The difference of 1 cc. of the soap solution=0.277.	
33.4 cc.	8.5
35.0 cc.	9.0
36.7 cc.	9.5
38.4 cc.	10.0
40.1 cc.	10.5
41.8 cc.	11.0
The difference of 1 cc. of the soap solution=0.294.	
43.4 cc.	11.5
45.0 cc.	12.0
The difference of 1 cc. of the soap solution=0.31.	

TABLE GIVING THE TENSION OF AQUEOUS VAPOR, FOR TEMPERATURES FROM 10°C. TO 25°C.

Temperature.	*Tension.*
10° C.	9.165 mm.
11° C.	9.792 mm.
12° C.	10.457 mm.
13° C.	11.162 mm.
14° C.	11.908 mm.
15° C.	12.699 mm.
16° C.	13.536 mm.
17° C.	14.421 mm.
18° C.	15.357 mm.
19° C.	16.346 mm.
20° C.	17.391 mm.
21° C.	18.495 mm.
22° C.	19.659 mm.
23° C.	20.888 mm.
24° C.	22.184 mm.
25° C.	23.550 mm.

TABLE OF SPECIFIC GRAVITIES CORRESPONDING TO DEGREES BEAUME.

1. *For Liquids Lighter Than Water Temp. 12.5° C.*

Deg. B.	Sp. Gr.	Deg. B.	Sp. Gr.	Deg. B.	Sp. Gr.
10	1.0000	27	.8957	44	.8111
11	.9932	28	.8902	45	.8066
12	.9865	29	.8848	46	.8022
13	.9799	30	.8795	47	.7978
14	.9733	31	.8742	48	.7935
15	.9669	32	.8690	49	.7892
16	.9605	33	.8639	50	.7849
17	.9542	34	.8588	51	.7807
18	.9480	35	.8538	52	.7766
19	.9420	36	.8488	53	.7725
20	.9359	37	.8439	54	.7684
21	.9300	38	.8391	55	.7643
22	.9241	39	.8343	56	.7604
23	.9183	40	.8295	57	.7565
24	.9125	41	.8248	58	.7526
25	.9068	42	.8202	59	.7487
26	.9012	43	.8156	60	.7449

2. *For Liquids Heavier Than Water. Temp. 17.5° C.*

Deg. B.	Sp. Gr.	Deg. B.	Sp. Gr.	Deg. B.	Sp. Gr.
0	1.0000	26	1.2153	51	1.5325
1	1.0068	27	1.2254	52	1.5487
2	.10138	28	1.2357	53	1.5652
3	1.0208	29	1.2462	54	1.5820
4	1.0280	30	1.2569	55	1.5993
5	1.0353	31	1.2677	56	1.6169
6	1.0426	32	1.2788	57	1.6349
7	1.0501	33	1.2901	58	1.6533
8	1.0576	34	1.3015	59	1.6721
9	1.0653	35	1.3131	60	1.6914
10	1.0731	36	1.3250	61	1.7111
11	1.0810	37	1.3370	62	1.7313
12	1.0890	38	1.3494	63	1.7520
13	1.0972	39	1.3619	64	1.7731
14	1.1054	40	1.3746	65	1.7948
15	1.1138	41	1.3876	66	1.8171
16	1.1224	42	1.4009	67	1.8398
17	1.1310	43	1.4143	68	1.8632
18	1.1398	44	1.4281	69	1.8871
19	1.1487	45	1.4421	70	1.9117
20	1.1578	46	1.4564	71	1.9370
21	1.1670	47	1.4710	72	1.9629
22	1.1763	48	1.4860	73	1.9895
23	1.1858	49	1.5012	74	1.0167
24	1.1955	50	1.5167	75	1.0449
25	1.2053				

WEIGHT OF ONE CUBIC CENTIMETRE OF MOIST NITROGEN IN MILLIGRAMMES.

t = Degrees Centigrade. *b* = Height of Barometer.

t	*b*. 726	728	730	732	734	736	738	740
5°	1.168	1.171	1.175	1.178	1.181	1.184	1.188	1.191
6°	1.163	1.167	1.170	1.173	1.176	1.179	1.183	1.186
7°	1.158	1.162	1.165	1.168	1.171	1.174	1.178	1.181
8°	1.153	1.157	1.160	1.163	1.166	1.169	1.173	1.176
9°	1.148	1.152	1.155	1.158	1.161	11.64	1.168	1.171
10°	1.143	1.147	1.150	1.153	1.156	1.159	1.163	1.166
11°	1.138	1.142	1.145	1.148	1.151	1.154	1.158	1.161
12°	1.133	1.136	1.140	1.143	1.146	1.149	1.152	1.155
13°	1.128	1.131	1.135	1.138	1.141	1.144	1.147	1.150
14°	1.123	1.126	1.129	1.133	1.136	1.139	1.142	1.145
15°	1.118	1.121	1.124	1.127	1.131	1.134	1.137	1.140
16°	1.113	1.116	1.119	1.122	1.125	1.129	1.132	1.135
17°	1.108	1.111	1.114	1.117	1.120	1.123	1.126	1.130
18°	1.102	1.105	1.109	1.112	1.115	1.118	1.121	1.124
19°	1.097	1.100	1.103	1.106	1.110	1.113	1.116	1.119
20°	1.092	1.095	1.098	1.101	1.104	1.107	1.110	1.113
21°	1.086	1.089	1.092	1.096	1.099	1.102	1.105	1.108
22°	1.081	1.084	1.087	1.090	1.093	1.096	1.099	1.102
23°	1.075	1.078	1.081	1.084	1.088	1.091	1.094	1.097
24°	1.070	1.073	1.076	1.079	1.082	1.085	1.088	1.091
25°	1.064	1.067	1.070	1.073	1.076	1.079	1.082	1.085
26°	1.058	1.061	1.064	1.067	1.070	1.073	1.076	1.079
27°	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074
28°	1.047	1.050	1.053	1.056	1.059	1.062	1.065	1.068
29°	1.041	1.044	1.047	1.050	1.053	1.056	1.059	1.062
30°	1.035	1.038	1.041	1.044	1.047	1.050	1.053	1.056

t	*b*. 742	744	746	748	750	752	754	756	758	760	762	764	766	768	770
5°	1.194	1.197	1.201	1.204	1.207	1.210	1.214	1.217	1.220	1.223	1.227	1.230	1.233	1.236	1.240
6°	1.189	1.192	1.196	1.199	1.202	1.205	1.209	1.212	1.215	1.218	1.222	1.225	1.228	1.231	1.234
7°	1.184	1.187	1.191	1.194	1.197	1.200	1.203	1.207	1.210	1.213	1.216	1.220	1.223	1.226	1.229
8°	1.179	1.182	1.186	1.189	1.192	1.195	1.198	1.202	1.205	1.208	1.211	1.214	1.218	1.221	1.224
9°	1.174	1.177	1.180	1.184	1.187	1.190	1.193	1.196	1.200	1.203	1.206	1.209	1.212	1.216	1.219
10°	1.169	1.172	1.175	1.178	1.182	1.185	1.188	1.191	1.194	1.198	1.201	1.204	1.207	1.210	1.214
11°	1.164	1.167	1.170	1.173	1.177	1.180	1.183	1.186	1.189	1.192	1.196	1.199	1.202	1.205	1.208
12°	1.159	1.162	1.165	1.168	1.171	1.174	1.178	1.181	1.184	1.187	1.190	1.193	1.197	1.200	1.203
13°	1.153	1.157	1.160	1.163	1.166	1.169	1.172	1.176	1.179	1.182	1.185	1.188	1.191	1.195	1.198
14°	1.148	1.152	1.155	1.158	1.161	1.164	1.167	1.170	1.174	1.177	1.180	1.183	1.186	1.189	1.192
15°	1.143	1.146	1.149	1.153	1.156	1.159	1.162	1.165	1.168	1.171	1.174	1.178	1.181	1.184	1.187
16°	1.138	1.141	1.144	1.147	1.150	1.154	1.157	1.160	1.163	1.166	1.169	1.172	1.175	1.178	1.182
17°	1.133	1.136	1.139	1.142	1.145	1.148	1.151	1.154	1.158	1.161	1.164	1.167	1.170	1.173	1.176
18°	1.127	1.130	1.133	1.137	1.140	1.143	1.146	1.149	1.152	1.155	1.158	1.161	1.164	1.168	1.171
19°	1.122	1.125	1.128	1.131	1.134	1.137	1.140	1.144	1.147	1.150	1.153	1.156	1.159	1.162	1.165
20°	1.116	1.120	1.123	1.126	1.129	1.132	1.135	1.138	1.141	1.144	1.147	1.150	1.153	1.156	1.160
21°	1.111	1.114	1.117	1.120	1.123	1.126	1.129	1.132	1.135	1.139	1.142	1.145	1.148	1.151	1.154
22°	1.105	1.108	1.111	1.115	1.118	1.121	1.124	1.127	1.130	1.133	1.136	1.139	1.142	1.145	1.148
23°	1.100	1.103	1.106	1.109	1.112	1.115	1.118	1.121	1.124	1.127	1.130	1.133	1.136	1.139	1.142
24°	1.094	1.097	1.100	1.103	1.106	1.109	1.112	1.115	1.118	1.121	1.124	1.128	1.131	1.134	1.137
25°	1.088	1.091	1.094	1.097	1.100	1.103	1.106	1.109	1.112	1.116	1.119	1.122	1.125	1.128	1.131
26°	1.083	1.086	1.089	1.092	1.095	1.098	1.101	1.104	1.107	1.110	1.113	1.116	1.119	1.122	1.125
27°	1.077	1.080	1.083	1.086	1.089	1.092	1.095	1.098	1.101	1.104	1.107	1.110	1.113	1.116	1.119
28°	1.071	1.074	1.077	1.080	1.083	1.086	1.089	1.092	1.095	1.098	1.101	1.104	1.107	1.110	1.113
29°	1.065	1.068	1.071	1.074	1.077	1.080	1.083	1.086	1.089	1.092	1.095	1.097	1.100	1.103	1.106
30°	1.059	1.062	1.065	1.068	1.070	1.073	1.076	1.079	1.082	1.085	1.088	1.091	1.094	1.097	1.100

TABLE OF SPECIFIC GRAVITY OF SULPHURIC ACID, TEMP. 15°C. REFERRED TO WATER AT 0°C.

Sp. Gr.	Per Cent. H_2SO_4	Sp. Gr.	Per Cent. H_2SO_4
1.007	1.9	1.308	40.2
1.014	2.8	1.320	41.6
1.022	3.8	1.332	43.0
1.029	4.8	1.345	44.4
1.037	5.8	1.357	45.6
1.045	6.8	1.370	46.9
1.052	7.8	1.383	48.3
1.060	8.8	1.397	49.8
1.067	9.8	1.410	51.2
1.075	10.8	1.424	52.6
1.083	11.9	1.438	54.0
1.091	13.0	1.453	55.4
1.100	14.1	1.468	56.9
1.108	15.2	1.483	58.3
1.116	16.2	1.498	59.6
1.125	17.3	1.514	61.0
1.134	18.5	1.530	62.5
1.142	19.6	1.540	64.0
1.152	20.8	1.563	65.5
1.162	22.1	1.580	67.0
1.171	23.3	1.597	68.6
1.180	24.5	1.615	70.0
1.190	25.8	1.634	71.6
1.200	27.1	1.652	73.2
1.210	28.4	1.671	74.7
1.220	29.6	1.691	76.4
1.231	30.9	1.711	78.1
1.241	32.2	1.732	79.9
1.252	33.4	1.753	81.7
1.263	34.7	1.774	84.1
1.274	36.0	1.796	86.5
1.285	37.4	1.819	89.7
1.297	38.8	1.842	100.0

TABLE SHOWING THE AMOUNT OF NITRIC ACID (HNO_3) CONTAINED IN SOLUTIONS OF DIFFERENT SPECIFIC GRAVITIES.

TEMP., 15 C. (URE).

Per Cent. HNO_3	Sp. Gr.	Per Cent. HNO_3	Sp. Gr.	Per Cent. HNO_3	Sp. Gr.
100	1.5000	66	1.3783	33	1.1895
99	1.4980	65	1.3732	32	1.1833
98	1.4960	64	1.3681	31	1.1770
97	1.4940	63	1.3630	30	1.1709
96	1.4910	62	1.3579	29	1.1648
95	1.4880	61	1.3529	28	1.1587
94	1.4850	60	1.3477	27	1.1526
93	1.4820	59	1.3427	26	1.1465
92	1.4790	58	1.3376	25	1.1403
91	1.4760	57	1.3323	24	1.1345
90	1.4730	56	1.3270	23	1.1286
89	1.4700	55	1.3216	22	1.1227
88	1.4670	54	1.3163	21	1.1168
87	1.4640	53	1.3110	20	1.1109
86	1.4600	52	1.3056	19	1.1051
85	1.4570	51	1.3001	18	1.0993
84	1.4530	50	1.2947	17	1.0935
83	1.4500	49	1.2887	16	1.0878
82	1.4460	48	1.2826	15	1.0821
81	1.4424	47	1.2765	14	1.0764
80	1.4385	46	1.2705	13	1.0708
79	1.4346	45	1.2644	12	1.0651
78	1.4306	44	1.2583	11	1.0595
77	1.4269	43	1.2523	10	1.0540
76	1.4228	42	1.2462	9	1.0485
75	1.4189	41	1.2402	8	1.0430
74	1.4147	40	1.2341	7	1.0375
73	1.4107	39	1.2277	6	1.0320
72	1.4065	38	1.2212	5	1.0267
71	1.4023	37	1.2148	4	1.0212
70	1.3978	36	1.2084	3	1.0159
69	1.3945	35	1.2019	2	1.0106
68	1.3882	34	1.1958	1	1.0053
67	1.3833				

TABLE OF SPECIFIC GRAVITY OF HYDROCHLORIC ACID.

TEMP. 15°C. (URE).

Sp. Gr.	Per Cent. HCl	Sp. Gr.	Per Cent. HCl	Sp. Gr.	Per Cent. HCl
1.2000	40.777	1.1328	26.913	1.0637	13.048
1.1982	40.369	1.1308	26.505	1.0617	12.641
1.1964	39.961	1.1287	26.098	1.0597	12.233
1.1946	39.554	1.1267	25.690	1.0577	11.825
1.1928	39.146	1.1247	25.282	1.0557	11.418
1.1910	38.738	1.1226	24.874	1.0537	11.010
1.1893	38.330	1.1206	24.466	1.0517	10.602
1.1875	37.923	1.1185	24.058	1.0497	10.194
1.1857	37.516	1.1164	23.650	1.0477	9.786
1.1846	37.108	1.1143	23.242	1.0457	9.379
1.1822	36.700	1.1123	22.834	1.0437	8.971
1.1802	36.292	1.1102	22.426	1.0417	8.563
1.1782	35.884	1.1082	22.019	1.0397	8.155
1.1762	35.476	1.1061	21.611	1.0377	7.747
1.1741	35.068	1.1041	21.203	1.0357	7.340
1.1721	34.660	1.1020	20.796	1.0337	6.932
1.1701	34.252	1.1000	20.388	1.0318	6.524
1.1681	33.845	1.0980	19.980	1.0298	6.116
1.1661	33.437	1.0960	19.572	1.0279	5.709
1.1641	33.029	1.0939	19.165	1.0259	5.301
1.1620	32.621	1.0919	18.757	1.0239	4.893
1.1599	32.213	1.0899	18.349	1.0220	4.486
1.1578	31.805	1.0879	17.941	1.0200	4.078
1.1557	31.398	1.0857	17.534	1.0180	3.670
1.1537	30.990	1.0838	17.126	1.0160	3.262
1.1515	30.582	1.0818	16.718	1.0140	2.854
1.1494	30.174	1.0798	16.310	1.0120	2.447
1.1472	29.767	1.0778	15.902	1.0100	2.039
1.1452	29.359	1.0758	15.494	1.0080	1.631
1.1431	28.951	1.0738	15.087	1.0060	1.124
1.1410	28.544	1.0718	14.679	1.0040	0.816
1.1389	28.136	1.0697	14.271	1.0020	0.408
1.1369	27.728	1.0677	13.863		
1.1349	27.321	1.0657	13.456		

SPECIFIC GRAVITY OF POTASSIUM AND SODIUM HYDROXIDE SOLUTIONS. TEMP. 15°C.

Sp. Gr.	Per Cent. KOH	Per Cent. NaOH	Sp. Gr.	Per Cent. KOH	Per Cent. NaOH
1.007	0.9	0.61	1.252	27.0	22.64
1.014	1.7	1.20	1.263	28.2	23.67
1.022	2.6	2.00	1.274	28.9	24.81
1.029	3.5	2.71	1.285	29.8	25.80
1.037	4.5	3.35	1.297	30.7	26.83
1.045	5.6	4.00	1.308	31.8	27.80
1.052	6.4	4.64	1.320	32.7	28.83
1.060	7.4	5.29	1.332	33.7	29.93
1.067	8.2	5.87	1.345	34.9	31.22
1.075	9.2	6.55	1.357	35.9	32.47
1.083	10.1	7.31	1.370	36.9	33.69
1.091	10.9	8.00	1.383	37.8	34.96
1,100	12.0	8.68	1.397	38.9	36.25
1.108	12.9	9.42	1.410	39.9	37.47
1.116	13.8	10.06	1.424	40.9	38.80
1.125	14.8	10.97	1.438	42.1	39.99
1.134	15.7	11.84	1.453	43.4	41.41
1.142	16.5	12.64	1.468	44.6	42.83
1.152	17.6	13.55	1.483	45.8	44.38
1.162	18.6	14.37	1.498	47.1	46.15
1.171	19.5	15.13	1.514	48.3	47.60
1.180	20.5	15.91	1.530	49.4	49.02
1.190	21.4	16.77	1.546	50.6	
1.200	22.4	17.67	1.563	51.9	
1.210	23.3	18.58	1.580	53.2	
1.220	24.2	19.58	1.597	54.5	
1.231	25.1	20.59	1.615	55.9	
1.241	26.1	21.42	1.634	57.5	

SPECIFIC GRAVITY OF AMMONIA SOLUTIONS. TEMP. 15°C.

LUNGE AND WIERNIK.

Sp. Gr.	Per Cent. NH_3	Sp. Gr.	Per Cent. NH_3
1.000	0.00	0.940	15.63
0.998	0.45	0.930	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

INDEX

Acidimetry 401, 424
Alkalies, determination of, in slags.186
in insoluble silicates............188
and alkaline corbonates........420
Alkalimetry 408, 416
Alkaline earths, qualitative test for 494
Alkaline earths, volumetric determination 422
Alum 108
Aluminum, determination as oxide.108
in pig iron, etc..................279
in insoluble silicates............194
in the presence of sulphuric acid.108
separation from barium.........135
separation from boric acid......176
separation from calcium.........................53, 135, 174, 186
separation from chromium......207
separation from cobalt......135, 186
separation from copper......135, 186
separation from iron.110, 123, 179, 214
separation from lead...........186
separation from magnesium......................123, 135, 150, 186
separation from manganese.....187
separation from mercury...247, 248
separation from phosphoric acid...........................124, 347
separation from potassium......108
separation from silicon......174, 194
separation from sodium.........174
separation from titanium.......290
separation from zinc............199
Aluminum, qualitative tests for.....................467, 490, 491, 492
Ammonia, determination as ammonium—platimic chloride.......109
as platium 110
in mineral water................347
in well water....................329
determination in guano.........361
colorimetric determination 327
volumetric determination...416, 456
separation from the metals......108
qualitative tests for........464, 498
Ammonium molybdate solution, for the determination of phosphoric acid 42
Analysis, qualitative, scheme for..463
by precipitation (volumetric)...454
by saturation...................408
Antimony, determination as pentasulphide 89
determination as trisulphide.... 78
indirect determination as barium sulphate 79
volumetric determination...233, 453
determination in antimony ores..233
determination in pig-iron.......288
separation as sodium antimonate 88
separation from arsenic......89, 91
separation from arsenic and tin. 95
separation from bismuth........263
separation from cadmium.......263
separation from cobalt.......... 22
separation from copper..................142, 187, 216, 222, 232, 263
separation from iron.93, 142, 232, 263
separation from lead.....78, 141, 222
separation from manganese.....263
separation from nickel......222,263
separation from selenium.......257
separation from silver..........222
separation fram tin..........87, 88
separation from vanadium......251
separation from zinc............263
metallic, analysis of............263
qualitative tests for........465, 468
Apparatus used in volumetric analysis 411
Arsenic, determination as ammonium-magnesium arsenate...... 96
determination as magnesium pyroarsenate 96
determination as pentasulphide.

..........................90, 97
determination as trisulphide..92, 93
in pig-iron 288
indirect determination as barium sulphate 92
volumetric determination....92, 449
separation from antimony....89, 91
separation from antimony and tin 95
separation from bismuth........222
separation from cadmium......260
separation from copper.........................186, 215, 220, 222
separation from lead............242
separation from selenium.......257
separation from tin..........90, 97
separation from vanadium.......257
qualitative tests for....465, 483, 484
Arsenic Acid, separation from phosphoric acid 243
qualitative test for.............484
Arsenopyrite 215
Arsenous acid in realgar and orpiment 449
qualitative tests for.........465, 484
Asbestos filter 14, 15
Ashes, analysis 356
Balance 7
Barite 62
Barium, determination as carbonate 25
determination as chromate...... 99
determination as sulphate....... 25
volumetric determination as barium chloride 456
separation from calcium........101
separation from magnesium....103
separation from strontium...... 99
separation from strontium and calcium 102
separation from sulphuric acid.. 62
qualitative test for.............494
Barium Chloride 25
Bases, separation of..............463
Beryllium, qualitative test for.....506
Bessemer slags 202
Bismuth, determination as basic nitrate 72
determination as oxide.......... 72
determination as oxychloride.71, 73
determination as metallic bismuth 73
separation from aluminum......186
separation from antimony.......262
separation from cadmium...76, 260
separation from copper...........................70, 250, 260, 265
separation from gold and cobalt..250
separation from iron.......186, 222
separation from lead.......71, 76, 77
separation from mercury....78, 246
separation from molybdenum...228
separation from nickel..........250
separation from phosphorus......28
separation from selenium.......251
separation from silver......260, 265
separation from tellurium.......250
separation from tin.......76, 77, 262
separation from vanadium.......224
separation from zinc............222
metallic, analysis of............270
qualitative tests for.468, 471, 472, 486
Bismuthinite 250
Borax bead, deportment of substances in 470
Boric acid, qualitative test for.....517
Bromine, qualitative test for.......464
Black copper 265
Blast furnace slag...............202
Blast lamp 9
Bog iron ore....................131
Bone black 365
Bone meal 364
Boracite 169
Boron, determination as potassium fluoborate 165
Boric Acid, determination of in the presence of hydrochtoric acid.168
determination of, in minerals....176
determination of, in mineral waters 341
determination of, in selicates....204
Bourmonite 234
Brass 63
Bromine, determination as silver bromide 46, 48, 52
gravimetric determination of, in the presence of iodine..47, 48, 49
volumetric determination of, in the presence of chlorine...46, 443
separation from chlorine and iodine 49
determination of, in mineral waters 341
Bronze Coins 67
Burettes 3, 414
Cadmium, determination as oxide. 77
determination as sulphide....... 76
separation from antimony.......257
separation from arsenic.........257
separation from bismuth........ 76

separation from copper.........142
separation from lead............ 76
separation from tin............. 76
separation from zinc............141
qualitative tests for.465, 469, 470, 487
Caesium, qualitative test for......497
Calamine 148
Calcite 21
Calcium, precipitation as oxalate.. 21
determination as carbonate..... 21
determination as oxide.......... 22
determination as sulphate.......102
volumetric determination........431
separation from the alkalies.....135
separation from aluminum......174
separation from barium.........101
separation from barium and strontium 102
separation from iron.54, 55, 119, 213
separation from magnesium..... ....54, 55, 103
separation from manganese.121, 149
separation from phosphoric acid. 149, 242
separation from strontium..101, 102
separation from tungsten.......254
separation from uranium........252
qualitative test for.............494
Calcium Carbonate 21
Carbide Carbon 312
Carbon, determination in pig-iron, etc 292-313
colorimetric determination in iron 311
determination in guano.........364
separation from silver chloride..228
Carbon dioxide, determination by direct weighing..........56, 59, 61
determination by loss...........381
determination in mineration water 336, 339, 340
determination in the presence of hydrogen sulphide 384
volumetric determination in carbonates 421
qualitative tests for.........467, 518
Carbon monoxide, qualitative test test for 464
Cerium, qualitative tests for..504, 506
Cerussite 236
Chalcopyrite 215
Chloric Acid, volumetric determination 445, 452
Chloride of Lime, technical valuation 443, 450
Chlorimetry 448
Chlorine, determination as silver chloride 26, 39
volumetric determination........ ....441, 450, 455
determination of, in the presence of bromine 46, 49
determination of, in substances insoluble in water............148
separation from iodine..44, 48, 49
volumetric determination of, in the presence of bromine......443
volumetric determination of, in the presence of iodine....441, 443
qualitative test for.............464
Chlorous Acid, volumetric determination 443
Chromic Acid, volumetric determination 433, 445, 451
Chromium, determination of, as lead chomate 39
determination of, as oxide....39, 43
determination in pig iron.......285
determination of, in insoluble silicates 206, 207
qualitative test for.........470, 471
separation from iron............205
separation from lead........... 43
separatiin from potassium....... 39
separation from uranium........253
Chrome Steel 271
Chromite 205
Cinnabar 246
Clay 195
Clay iron ore....................127
Coal, proximate analysis..........374
ultimate analysis 378
determination of heating effect..378
Cobalt, determination as cobaltous oxide 33
determination as metallic cobalt 33
volumetric determination of cobaltic oxide 452
separation from iron.........69, 136
separation from manganese.....136
separation from nickel.33, 34, 35, 36
separation from zinc............219
qualitative tests for....469, 470, 472
Cobalt Sulphate 33
Cobaltite 236
Colorimeter, Duboscq 326
Copper, determination as cupric oxide 22
determination as metallic copper 71
determination as sulphocyanate.. 23

determination as cuprous sulphide 66
electrolytic determination 218
volumetric determination........ ....216, 217, 447, 454
determination in pig-iron, etc...287
separation from antimony....... ....142, 186, 216, 222, 232, 262
separation from arsenic......... ....186, 215, 219, 222
separation from bismuth........ 70
separation from cadmium.......141
separation from cobalt and nickel 68, 73
separation from iron.67, 122, 186, 213
separation from lead............141
separation from phosphorus..... 82
separation from silver.......... 66
separation from tin...........67, 83
separation from tungsten.......251
separation from zinc..63, 67, 73, 142
qualitative tests for....468, 470, 472
Copper matte 217
Copper slags 186
Copper speise 222
Copper sulphate 22
Cupola slags 202
Cuprous oxide, determination in refined copper 268
Cyanides, qualitative test for......466
Datolite 176
Decantation 11
Decomposition of substance by fusion 9, 476
Dessicator 5
Diamond mortar 4
Didymium, qualitative detection... ....504, 506
Dolomite 53
Drying substances 5
Eau de Javelle, valuation of.......450
Electrolysis 1
Elutriation 5
Epidote 199
Erbium, qualitative tests for..504, 507
Feldspar 194
Ferro-manganese 271
Ferro-silicon 271
Ferrous sulphate 24
Filter paper 16
Filtration 11, 13
Flame colorations 473
Flourine, determination as calcium fluoride 150
gasometric determination 153
volumetric determination 152
determination in mineral water.341
determination in the presence of phosphoric acid 150
qualitative test for..............515
Furnace bears 228
Galenite 237
Gangue, determination in the presence of silica 127, 197
German silver 73
Glass 198
Glaucodote 23
Gold, determination in pyrite.....212
determination in the dry way....239
separation from molybdenum....228
separation from silver..........239
separation from tellurium.......250
separation from vanadium......228
qualitative tests for....468, 482, 485
Gooch crucible 14
Graphitic carbon, determination in pig-iron 312
Gravimetric analysis 1
Green Vitriol 24
Group reagents, deportment of the acids with 509
deportment of the bases with...478
Guano 360
Gunpowder 388
Hard lead 262
Hematite 122
Hydrogen sulphide, determination.181
determination in mineral water. 334, 335
determination in the presence of carbon dioxide 384
determination in the presence of sulphuric acid 335
volumetric determination........ ....334, 433, 447, 452
Hydriodic acid, volumetric determination 425
qualitative test for..............514
Hydrochloric acid, qualitative test for 513
Hydrobromic acid, qualitative test for 514
Hydrofluoric acid, qualitative tests for 474, 515
Hydrogen, determination of, in organic substances 390
preparation 31
Hydrogen sulphide, qualitative tests for 464, 512
Hypochlorous acid, volumetric de-

  - termination ... 443, 450
- Ilvaite ... 178
- Indicators ... 408
- Indium, qualitative tests for ... 468, 479, 507
- Iodic acid, volumetric determination ... 446
- Iodine, determination as palladous iodide ... 44
  - determination as thallous iodide. 45
  - volumetric determination ... 440
  - determination in mineral waters. 340
  - determination in phosphorites ... 158
  - determination in the presence of bromine ... 45
  - determination in the presence of chlorine ... 44, 441
  - qualitative test for ... 464
  - separation from bromine .. 46, 47, 48
  - separation from chlorine .. 44, 45, 49
  - separation from bromine and chlorine ... 49
- Iridium, qualitative tests for ... 469, 499
- Iron, determination as oxide ... 24, 54
  - determination in pig-iron ... 288
  - ferric, determination in iron ores. ... 128, 129
  - ferric, volumetric determination of, with stannous chloride. 122, 434
  - ferrous, determination in well water ... 316
  - ferrous, determination in mineral water ... 336
  - ferrous, determination in the presence of ferric ... 113
  - ferrous, determination in insoluble silicates ... 200
  - ferrous, volumetric determination with patassium bichromate ... 113
  - ferrous, volumetric determination with potassium permangnate .. 111
  - ferrous, determination in iron ores ... 111, 128
  - metallic, determination in slags. 183
  - qualitative test for ... 490
  - separation from aluminum ... 110, 123, 179, 213, 275
  - separation from aluminum, calcium, cobalt, copper, chromium, lead, magnesium, manganese, nickel, titanium and zinc .. 213, 275
  - separation from antimony and tin ... 93
  - separation from calcium and magnesium ... 54, 55, 119, 213, 275
  - separation from chromium ... 205
  - separation from cobalt and nickel ... 68, 135
  - separation from copper ... 67, 122, 186, 213
  - separation from manganese ... 119, 120, 135, 143, 213, 275
  - separation from molybdenum ... 228
  - separation from phosphorus ... 228
  - separation from titanium ... 124, 125
  - separation from tungsten ... 254
  - separation from zinc ... 64, 67, 143
  - separation from zirconium ... 209
- Kaolin ... 195
- Kipp's apparatus ... 31
- Lanthanum, qualitative tests for 504, 506
- Lead, determination as chloride. 43, 141
  - determination as sulphate ... 63
  - determination as sulphate ... 63
  - determination as sulphide ... 44
  - determination in the dry way ... 238
  - volumetric determination ... 432
  - qualitative test for ... 468, 486
  - separation for antimony ... 78, 222
  - separation from arsenic ... 242
  - separation from bismuth ... 72, 76, 78
  - separation from cadmium ... 76
  - separation from chromium ... 43
  - separation from copper ... 142
  - separation from gold ... 239
  - separation from iron ... 214
  - separation from mercury ... 78
  - separation from molybdenum ... 241
  - separation from phosphoric acid. 203
  - separation from selenium ... 251
  - separation from silver ... 237
  - separation from silicon ... 141
  - separation from sulphur ... 222
  - separation from tin ... 68, 76, 78
  - separation from vanadium ... 162
  - separation from zinc ... 70, 141
  - separation from zinc, iron and nickel ... 63
- Lead chromate ... 43
- Lead dioxide, determination in the presence of lead monoxide ... 244
- Lead matte ... 219
- Lead monoxide, determination of in the presence of lead dioxide ... 244
- Lead peroxide, volumetric determination ... 446
- Lead slags ... 186
- Lead speise ... 222
- Lead sulphate, determination in the

presence of silicic acid........238
Limonite 131
Linnaeite 236
Lithium, determination as sulphate 139
determination in mineral water.352
determination in insoluble silicates 188
qualitative detection 481, 497
separation from potassium and sodium 139
Magnetite 128
Marble 21
Magnesium, determination as oxide 28, 106
determination as pyrophosphate. 27
qualitative test for.............495
separation from the alkalies.105, 107
separation from the alkaline earths 103
separation from calcium........ 54
separation from iron.......................54, 55, 119, 120, 213
Magnesia mixture 41
Magnesium sulphate 27
Manganese, determination as trimanganese tetroxide ...37, 38, 39
determination as sulphate....... 39
determination as sulphide....... 39
determination in iron ores, pig-iron, etc., by Hampe's method.281
Julien's method 282
Volhard's method 114, 280
qualitative tests for........470, 492
separation from calcium....121, 148
separation form cobalt and nickel 136
separation from iron....................119, 120, 136, 143, 214, 282
separation from tungsten.......254
separation from zinc.........85, 143
Manganic acid, qualitative test for.492
volumetric determination.......446
Manganese dioxide, determination.131
volumetric determination 134, 446, 452
Manganous chloride 37
Mercury, determination as metallic mercury 227, 247
determination as mercurous chloride 247
determination as mercuric sulphide 78, 247
determination in cinnabar..247, 248
qualitative tests for........465, 482
separation from bismuth........ 78
separation from lead........... 78
separation from tin............. 78
Molybdenum, determination 228
qualitative tests for........469, 499
separation from lead........... 240
separation from phosphoric acid.232
separation from tungsten.......256
separation from vanadium......229
Molybdenite 249
Molybdic acid, volumetric determination 241
Natrolite 174
Nessler's reagent 498
Nickel, determination as metallic nickel 35
determination as nickelous oxide 34, 35, 36, 68, 75
qualitative tests for.469, 470, 471, 472
separation from cobalt.33, 34, 35, 36
separation from copper.......68, 73
separation from iron........69, 136
separation from manganese.....136
separation from zinc......65, 69, 76
metallic, analysis of............271
Nickel coins 68
Nickel, cube 271
Nickel matte 219
Niccolite 235
Niobic acid, qualitative tests for.......................467, 504, 505
Niter 387
Nitric acid, volumetric determination 424, 433
determination in mineral water.346
determination in niter..........387
determination in well water....323
qualitative test for.............513
Nitrogen, determination 398
determination, absolute 401-406
determination, Kjeldahl's method 366
determination in fertilizers.....401
determination in pig-iron.......313
qualitative test for.............389
Nitrous acid, in well water, colorimetric determination 326
qualitative test for 513
Normal solutions 407
Olivine 177
Organic compounds, analysis of............................389, 406
deportment in preliminary tests.466
Organic matter, determination in well water 330
Orpiment, determination of arsenous acid in..................449

Osmium, qualitative tests for. 502, 503
Oxalic acid, determination in guano ... 365
  influence of in tests ... 491, 492, 493
Oxidation and reduction, analysis by ... 410, 427
Oxygen, determination in organic matter ... 390
  determination in peroxides ... 139
  qualitative test for ... 464
Palladium, qualitative test for ... 503
Pearl ash ... 386
Permanganic acid qualitative test for ... 492
Pig-iron ... 271
Phosphorus, determination in alloys ... 85
  determination of, in pig-iron, etc. .298
  determination in iron ores ... 124
  volumetric determination in pig-iron, etc. ... 299
Phosphoric acid, determination as magnesium pyrophosphate ... 41
  determination in phosphorites. .159
  determination in the presence of metals ... 149
  indirect determination with ammonium-phospho molybdate ... 41
  determination in guano ... 361
  reverted, determination in superphosphates ... 371
  separation from aluminum ... 124
  separation from arsenic acid ... 243
  separation from fluorine ... 150
  separation from molybdenum ... 232
  separation from sodium ... 42
  soluble, determination of, in superphosphates ... 370
  volumetric determination ... 159, 457
Phosphor bronze ... 82
Phosphor-manganese bronze ... 83
Phosphoric acid, separation from vanadium ... 162, 232
  separation from tin ... 83, 84
  qualitative test for ... 512
Phosphorite ... 148
Platinum, qualitative test for ... 469, 482, 499
Platinum ware, care of ... 19
Porcelain ... 198
Potassium ferrocyanide, volumetric determination of ... 432
  determination as chloride ... 40
  determination as potassium-platinic chloride ... 104
  determination as sulphate ... 106
  volumetric determination as potassium acid tartate ... 426
  volumetric determination as potassium fluosilicate ... 426
  determination in insoluble silicates ... 188
  determination in mineral water. 351
  determination in the presence of heavy metals ... 138
  determination in the presence of sodium ... 105, 107
  qualitative tests for ... 497
  separation from aluminum ... 108
  separation from calcium ... 135
  separation from chromium ... 39
  separation from lithium ... 138
  separation from magnesium. 105, 107
  separation from the non-alkaline bases with barium hydroxide ... 351
  separation from phosphoric acid. 148
  separation from sodium ... 103
Potassium sichromate ... 39
Potassium permanganate, standardization ... 429, 431
Precipitates, treatment of ... 10-20
Precipitation ... 10
Prehnite ... 175
Preliminary tests ... 464
Proustite ... 225
Psilomelane ... 135
Pulverization ... 4
Pyrargyrite ... 225
Pyrites ... 210
Pyromorphite ... 242
Realgar, determination of arsenous acid ... 449
Red lead, valuation ... 244
River water ... 315
Refined copper ... 268
Refined lead ... 257
Refining slag ... 183
Rhodium, qualitative tests for. 469, 502
Roasted pyrites ... 213
Rubidium, qualitative test for. 497, 498
Ruby silver one ... 225
Ruthenium, qualitative test for ... 502
Salt of phosphorus bead, deportment of substances in ... 471
Saltpeter ... 387
Scheelite ... 257
Selenium, determination ... 251
  determination in pyrites ... 212
  separation from antimony, arsenic, barium, bismuth, cal-

cium, cobalt, copper, iron, lead, magnesium, nickel, silver, silicon, strontium and vanadium..251
qualitative test for.............499
Selenic acid, interference in test for sulphuric acid.............511
volumetric determination. (See iodates) 446
Siderite 111
Sifting 4
Silver, determination as chloride.. 66
determination as metallic silver.261
determination in the dry way... ....237, 238, 245
determination in the presence of gangue 237
determination in red lead.......245
volumetric determination 454
qualitative tests for.468, 470, 471, 486
separation from antimony and arsenic 222
separation from bismuth....260, 265
separation from cadmium.......260
separation from carbon.........231
separation from copper......66, 250
separation from gold............239
separation from iron............222
separation from lead.......238, 260
separation from mercury........249
seperation from molybdenum....228
separation from phosphorus.....228
separation from selenium 251
separation from sulphur........222
separation from vanadium......228
separation from zinc............222
metallic analysis of.............270
Silver coins 66
Silicates 169
Silicates, decomposition with acid under pressure................193
decomposition with boric oxide.191
Silicic acid, determination 53
determination in the pesence of gangue 127, 197
determination in insoluble silicates 187, 191, 193
determination in soluble silicates 169
qualitative test for.............516
separation from the alkalies.....188
separation from aluminum..169, 206
separation from aluminum, calcium, iron and magnesium..... 53
separation from barium......62, 186
separation from boric acid in silicates 204
separation from calcium....169, 206
separation from carbon.........264
separation from fluorine........148
separation from iron...........196
separation from lead........141, 237
separation from magnesium.169, 206
separation from manganese.175, 199
separation from silver..........237
separation from sulphur.....62, 179
separation from tin 198
separation from titanium....124, 173
separation from tungsten.......254
Silicon, determination in ferro-silicon 272
See also Silicic acid.
determination in pig-iron...272, 273
Slags 183, 186, 202
Soap 386
Soda ash, valuation...............381
Soft solder 68
Solution of the substance.......8, 474
Specific gravity of mineral water, determination 337, 338
Spelter 263
Sphalerite 141
Spiegeleisen 271
Spring water 315
Stannic oxide, qualitative test for. 467, 484, 485
Stannous oxide, qualitative test for.485
Steam-Bath 9
Sodium, determination as chloride. 42
determination of hydroxide in the presence of carbonate.........384
determination in mineral water.351
determination of, in the presence of aluminum 174
determination of in the presence of potassium 103
indirect determination in the presence of potassium....105, 107
volumetric determination as corbonate 381
qualitative test for..............497
separation from lithium.........138
separation from magnesium.105, 107
separation from phosphoric acid. 42
volumetric determination as carbonate 381
volumetric determination as chloride 455
volumetric determination as sodium fluosilicate 426
Sodium arsenite and iodine........448

Sodium phosphate 40
Sodium thiosulphate, volumetric determination 440
Sodium thiosulphate and iodine....437
Steel 265
Stibnite 232
Strontium, determination as sulphate 102, 103
  volumetric determination 456
  qualitative test for..............494
  separation from barium......... 99
  separation from calcium........101
  separation from barium and calcium 102
  separation from magnesium.....103
  separation from sulphuric acid..103
Sulphur, determination as barium sulphate 23, 63
  free, determination of...........180
  determination in sulphides...... ....147, 181, 210, 237, 246
  determination in insoluble silicates 222
  determination in coal...........376
  determination in zinc...........265
  determination in pig-iron....291-297
  in iron, colorimetric determination 297
  qualitative tests for.........464, 512
  separation by volatilization as chloride 222
  separation from antimony..221, 232
  separation from carbon.........388
  separation from cobalt..........222
  separation from copper..........222
  separation from lead.......222, 232
  separation from nickel, silver, bismuth, zinc 222
  separation from silicon..........179
Sulphuric acid, determination in the presence of ferric iron.24, 124
  determination in iron ores.......124
  concentrated, deportment of substances with..................473
  determination in insoluble substances 62
  determination in the presence of aluminum. 108
  determination in the presence of hydrogen sulphide 335
  qualitative test for.............511
  separation from barium, strontium and calcium..........62, 103
  separation from iron...........232
  separation from silicic acid..... 63
  volumetric determination 321, 424, 457
Sulphurous acid, qualitative tests for 464, 511
Superphosphates 369
Tantalic acid, qualitative tests for. 467, 504, 505
Tellurium, determination 250
  qualitative tests for....465, 469, 500
  separation from arsenic, antimony, bismuth, cobalt, copper, gold, iron and nickel............250
Temper carbon, determination in iron 313
Tetrahedrite 226
Thallium, qualitative tests for.468, 507
Thiosulphuric acid, determination. 335, 382, 440
Tin ore 149
Titanium, determination in pig-iron 290
  separation from aluminum, chromium, iron, phosphorus and silicon 124, 125, 173, 290
Titanic acid, determination in insoluble silicates 173
  determination in iron ores.......124
  qualitative tests for....470, 471, 472
Tourmaline 204
Tungsten, determination 254
  determination in pig-iron, etc....284
  separation from calcium, copper, iron, magnesium, manganese, silicic acid and tin....254, 257, 284
  separation from molybdenum....257
  qualitative tests for............ ....467, 469, 470, 471, 472, 501
Tungsten steel 271
Type metal 78
Tin, determination as oxide.....67, 83
  indirect determination as barium sulphate 84
  determination in bronze......... 86
  determination in glass..........198
  determination in tin ore.........140
  qualitative tests for........468, 484
  separation from antimony.87, 88, 95
  separation from arsenic...88, 95, 97
  separation from bismuth......76, 77
  separation from cadmium....76, 262
  separation from copper.......67, 83
  separation from iron.........93, 209
  separation from lead......68, 76, 77
  separation from manganese and nickel 84, 143

separation from mercury........ 77
separation from phosphoric acid. 83, 84
separation from silicic acid.....198
separation from tungsten...255, 256
separation from zinc............ 67
metallic 269

Ulexite 164
Ullmannite 235
Ultimate analysis 378, 390
Uraninite 251
Uranium, determination in uranite 252
qualitative test for 490
separation from the alkaline earths, chromium, iron, cobalt, manganese, magnesium, nickel and zinc 251
Uric acid, determination in guano.366
Ultramarine 179
Vanadinite 162
Vanadium, determination.162, 229, 251
volumetric determination (see iodates 441) 163, 230
determination in pig-iron........285
determination in the presence of molybdenum 230
qualitative test for.........499, 501
separation from antimony and arsenic 251
separation from calcium........251
separation from cobalt and copper 228
separation from gold............228
separation from iron 228, 251
separation from lead...........228
separation from manganese.....251
separation from nickel, silver and bismuth 228
separation from phosphoric acid. 162, 232
separation from tin.............251
Volumetric analysis 3, 407
Water, determination by loss...... ....25, 131, 140
direct determination.........61, 110
determination in silicates.......171
determination in the presence of ammonia 110, 360
determination in the presence of organic matter 176
determination of total hardness.319
determination of permanent hardness 320
determination in coal............374
determination in guano.........360
determination of specific gravity. 337, 338
Water-bath 9
Well water 315
White vitriol 29
Wolframite 254
Wood's metal 76
Work-lead 262
Wulfenite 241
Yttrium, qualitative tests for..504, 506
Zinc 263
determination as oxide.......29, 64
determination as sulphide.....30. 64
volumetric determination...145, 146
determination in zinc ores.......144
qualitative test for.....467, 469, 493
separation from aluminum..143, 199
separation from antimony, arsenic and tin..............219, 263
separation from bismuth........222
separation from cadmium.......141
separation from cobalt.....219, 222
separation from copper......... ....63, 67, 73, 142, 222
separation from iron............ ....65, 67, 75, 143, 186, 213, 219
separation from lead.63, 70, 141, 219
separation from magnesium.....141
separation from manganese...... 83
separation from nickel.......... ....67, 70, 75, 219
separation from phosphorus.202, 228
separation from silver..........222
separation from tin..........67, 262
separation from uranium.......251
separation from vanadium..228, 251
Zinc blende 141
Zinc dust, valuation...............265
Zinc silicates 148
Zinc sulphate 29
Zinkenite 234
Zircon 209
Zirconium, determination in insoluble silicates 209
qualitative test for.....504, 506, 507

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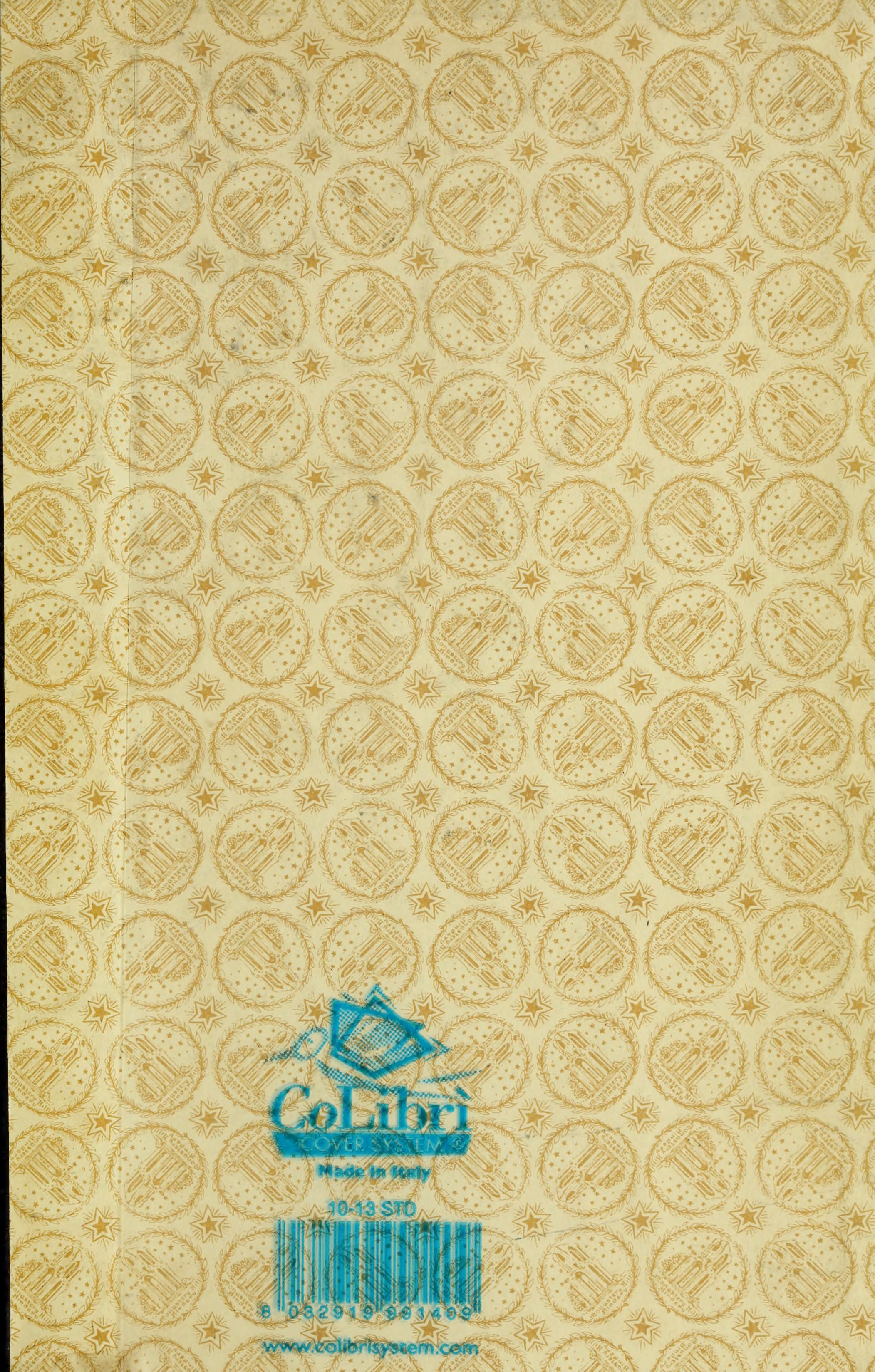

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